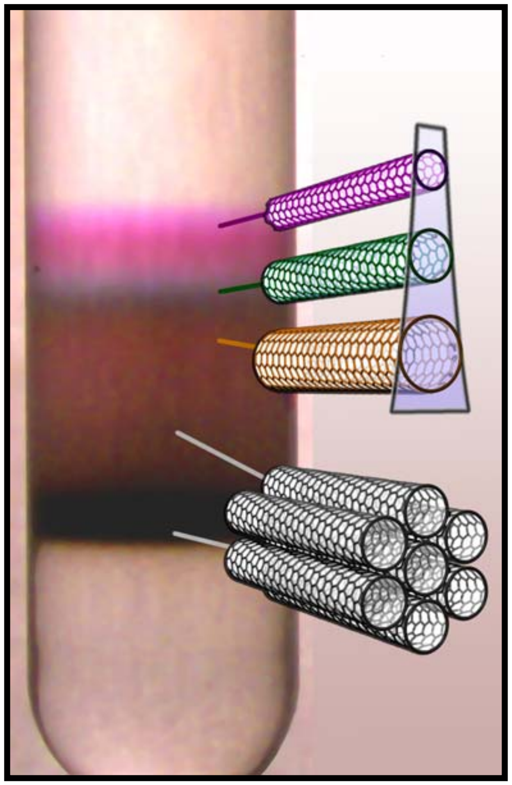
Sorting single-walled carbon nanotubes by their physical and electronic structure using density differentiation



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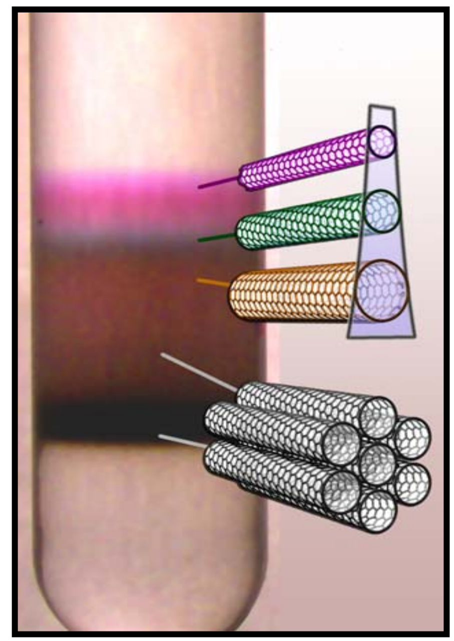
3rd NASA-NIST Workshop
on Nanotube Measurements

Gaithersburg, Maryland
September 26, 2007

Outline

- Motivation and background information
- Density gradient centrifugation of DNA encapsulated SWNTs
- Density gradient centrifugation of surfactant encapsulated SWNTs
- Applications and commercialization



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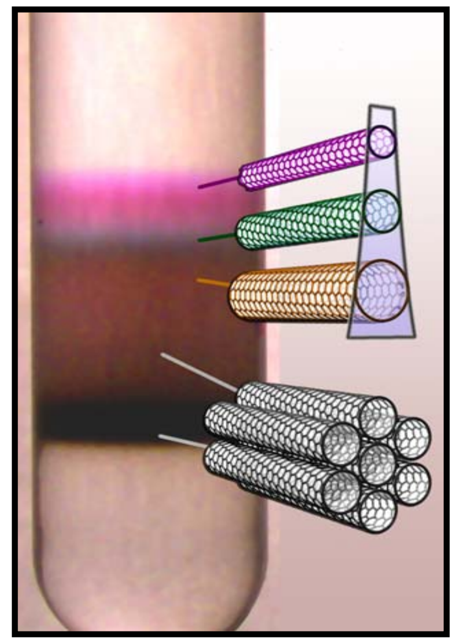
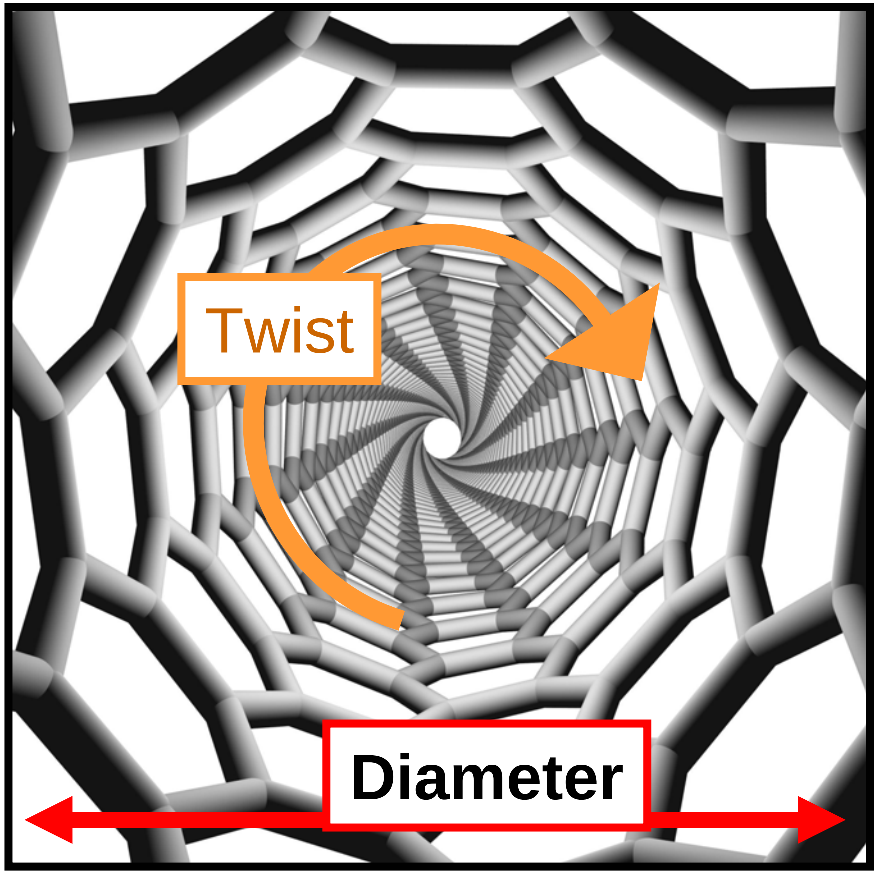


Carbon Nanotube Polydispersity

- ***<u>Many</u>*** chiralities are produced during current methods of SWNT synthesis.
- ***<u>Chirality (twist and diameter) determine electronic and optical properties</u>*.**
- Bulk quantities of carbon nanotubes pure in one chirality would likely enable:
  - SWNT optical amplifiers
  - SWNT thin film transistors
  - SWNT transparent conductors
  - SWNT multi-analyte biosensors

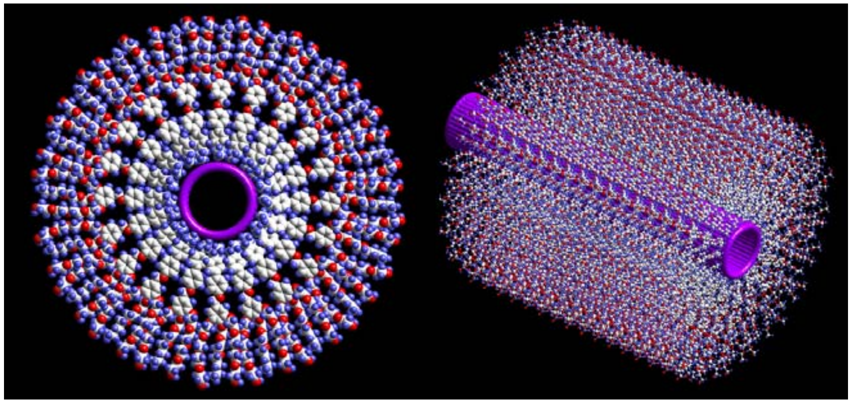


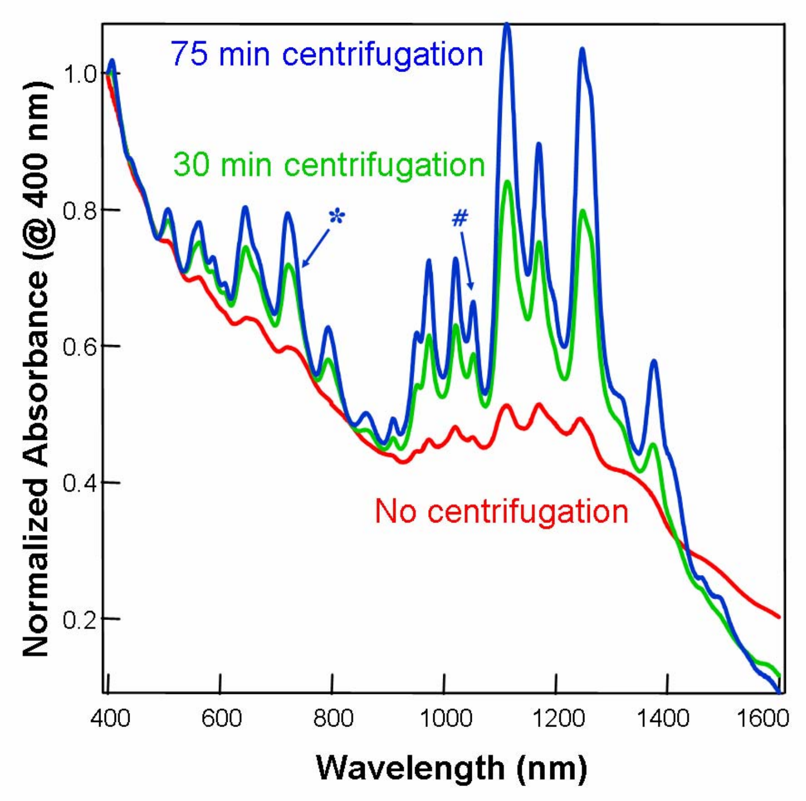
Conventional Centrifugation of SWNTs

Nano Letters, **3**, 1549 (2003).

- Raw SWNTs are suspended in an amphiphilic surfactant (e.g., sodium dodecyl sulfate, DNA, sodium cholate, etc.) in heavy water by horn ultrasonication.

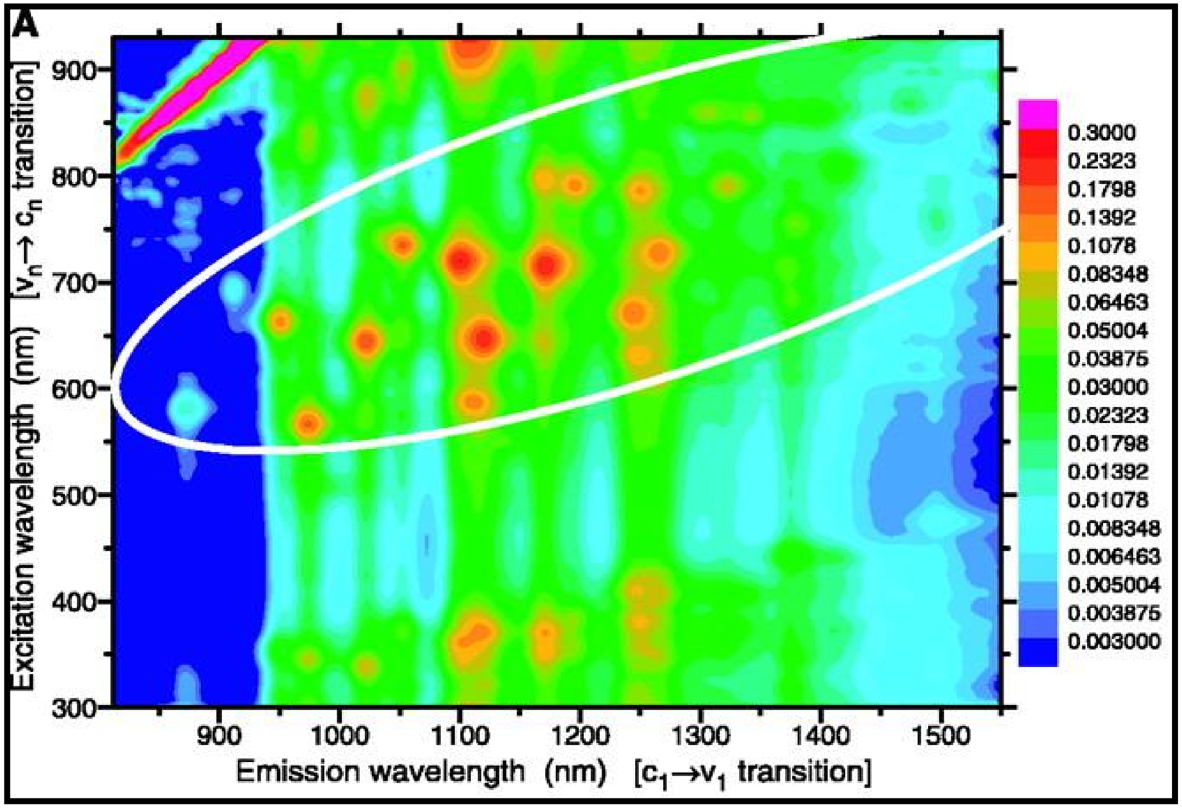
- Aggregations of nanotubes are removed by centrifugation.





The nanotube optical absorbance and fluorescence spectra become sharper as bundles are removed by centrifugation.

Conventional Centrifugation Removes Bundles but Polydispersity Remains



[1] M.J. O'Connell et al., *Science* **297**, 2002.

[2] S. Bachilo et al., *Science* **298,** 2002.

[3] A. Hagen et al., *Nano Lett.* **3**, 2003.

[4] J-S. Lauret et al., *PRL* **90**, 2003.

Each peak in the PL spectrum represents a different SWNT chirality.

→

A clear need exists for sorting SWNTs by their physical and electronic structure

Previous Strategies for Sorting SWNTs

- Metallic-semiconducting isolation
  - Dielectrophoresis[1] (electrical)
  - Chemical reactivity[2,3] (chemical)
  - Anion exchange[5] (charge)
  - Controlled electrical breakdown[4] (electrical)
- Diameter sensitivity
  - Anion exchange[5] (charge)

[1] R. Krupke *et al. Science* **301**, 2003.
[2] M. S. Strano *et al. Science* **301**, 2003.
[3] G. G. Samsonidze, *Appl. Phys. Lett.* **85**, 2004.
[4] P.G. Collins, M.S. Arnold, P. Avouris, *Science*, 2001.
[5] M. Zheng *et al. Nature Mater*. **2**, 2003.

Desired Attributes of a SWNT Purification Process

- Scalable
- Compatible with SWNTs of all lengths and diameters
- Utilizes non-covalent/reversible functionalization
- Iteratively repeatable
- Economical

We found that none of the pre-existing purification strategies sufficiently met all of these criteria.

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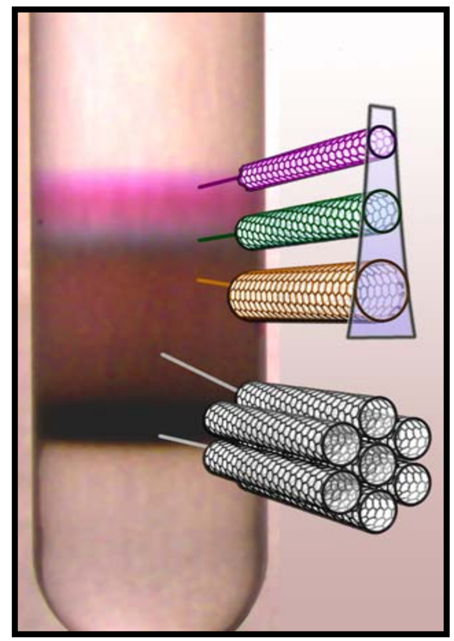


SWNT Density as a Function of Diameter

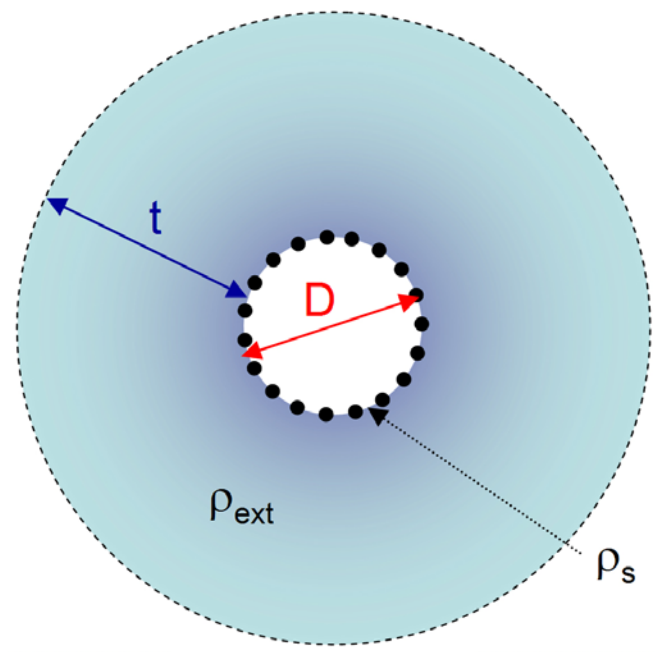
Nano Letters, **5**, 713 (2005).

Without external functionalization/hydration:

$$\boxed{\rho_{NT} := \frac{4\,\rho_s}{D}}$$

Including external functionalization/hydration:

$$\boxed{\rho_{NT} := \frac{\rho_s\,\pi\,D + \rho_{ext}\,\pi\left(\left(\frac{D}{2}+t\right)^2 - \frac{D^2}{4}\right)}{\pi\left(\frac{D}{2}+t\right)^2}}$$



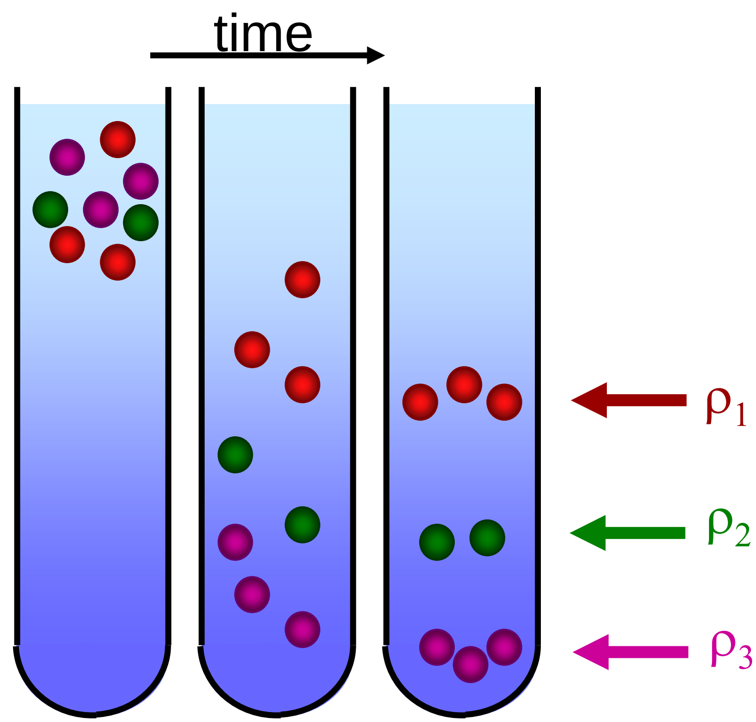
For small diameters, SWNT density was expected to vary by < 1% between adjacent SWNT diameters.

Separation in Density Gradients

Nano Letters, **5**, 713 (2005).

$$v = \frac{d^2(\rho_p - \rho_l)g}{18\mu}.$$

$$\mathbf{g = \omega^2 r}$$



v = particle velocity

d = particle size

µ = viscosity

g = centrifugal force

r = density

A preformed density gradient is used, and particles move towards equilibrium, where their density matches that of the local density of the gradient.

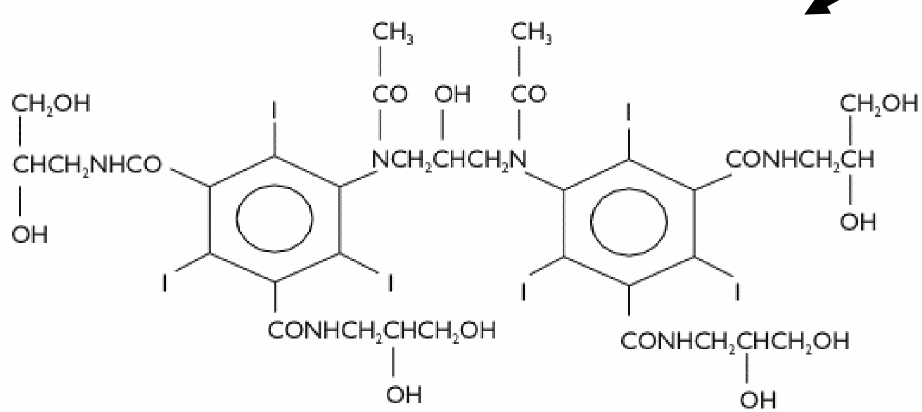
Density Gradient Media

Nano Letters, **5**, 713 (2005).

Table 8.1. Buoyant density (g/ml^{-1}) of macromolecules in density gradient media

Macromolecule	CsCl	Cs_2SO_4	Metrizamide	Nycodenz®	Iodixanol
Native DNA	1.71	1.43	1.12	1.13	1.12
Denatured DNA	1.73	1.45	1.14	1.17	1.16
RNA	>1.9	1.64	1.17	1.18	1.18
Polysaccharides	1.62		1.28	1.29	
Proteins	1.3	1.3	1.27	1.27	1.26
Proteoglycans		1.46			

Data from Ford and Rickwood (1983), Rickwood (1992) and Rickwood and Patel (1996).



DNA-Wrapped Carbon Nanotubes

- Single-stranded DNA

  1 mg ssDNA: 1 mg NT: 1 mL 0.1 M NaCl -- ultrasonicate
- Sequences 20-60 bases long, rich in G,C, and T work best
  - We use $GT_{(20)}$

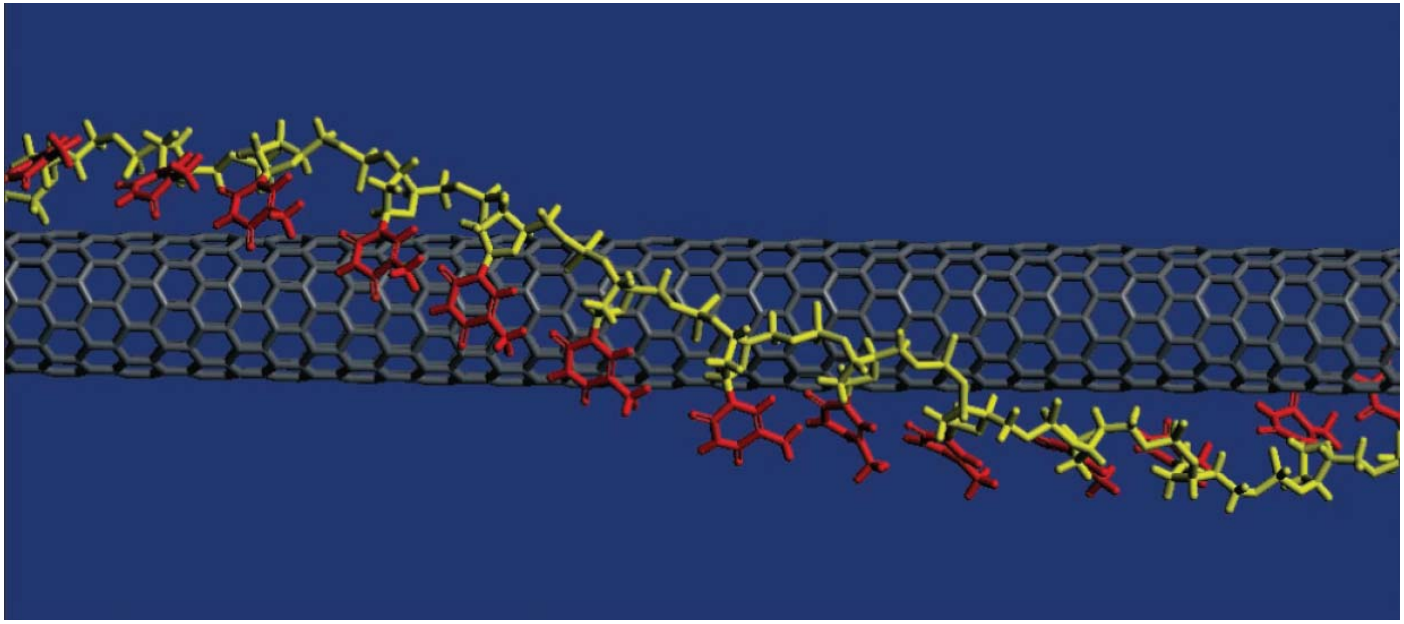
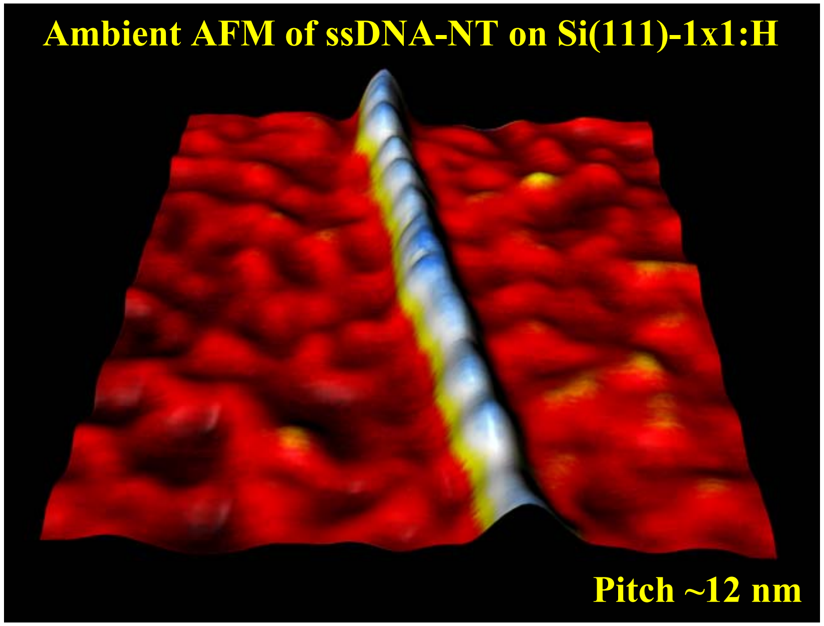
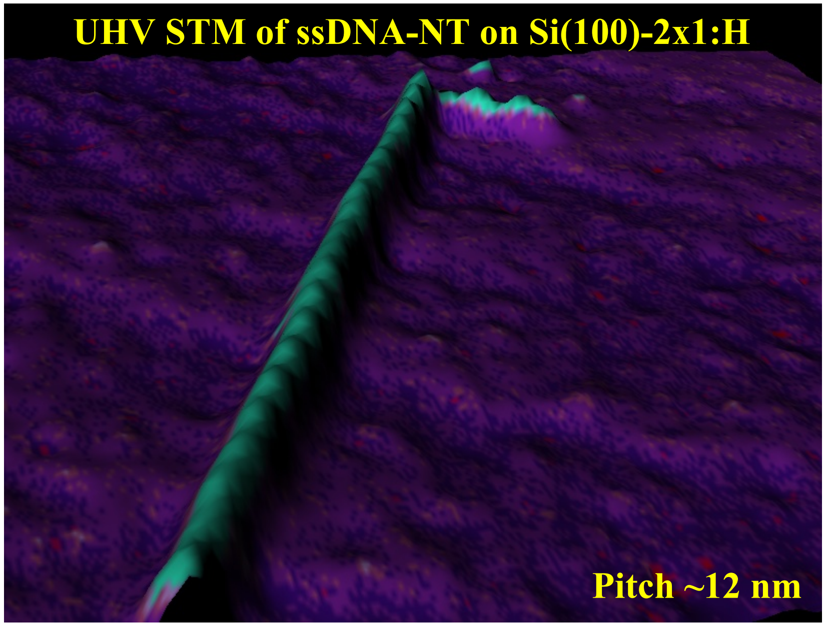


Figure and method from M. Zheng *et al. Nature Materials* 2003.

Imaging DNA-Wrapped SWNTs



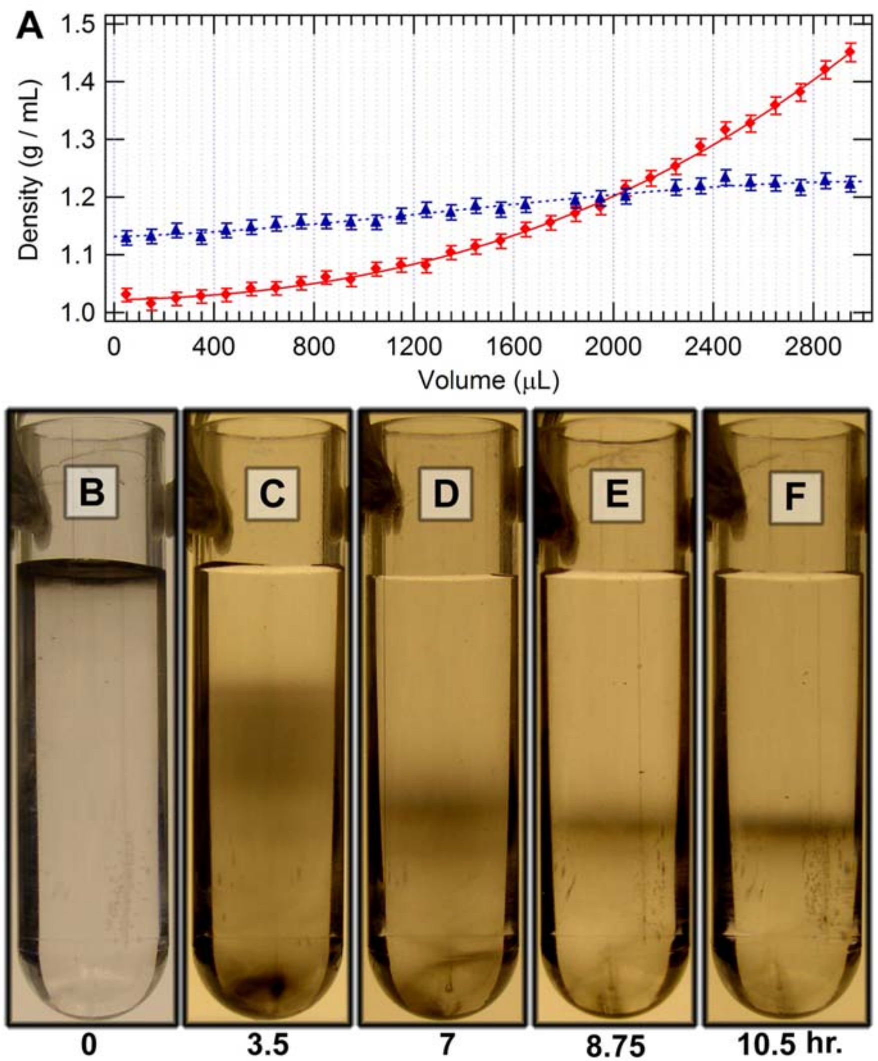


• Scanning probe microscopy images are consistent with the proposed helical wrapping of DNA around the SWNT.

Density Gradient Ultracentrifugation (DGU)

Nano Letters, **5**, 713 (2005).

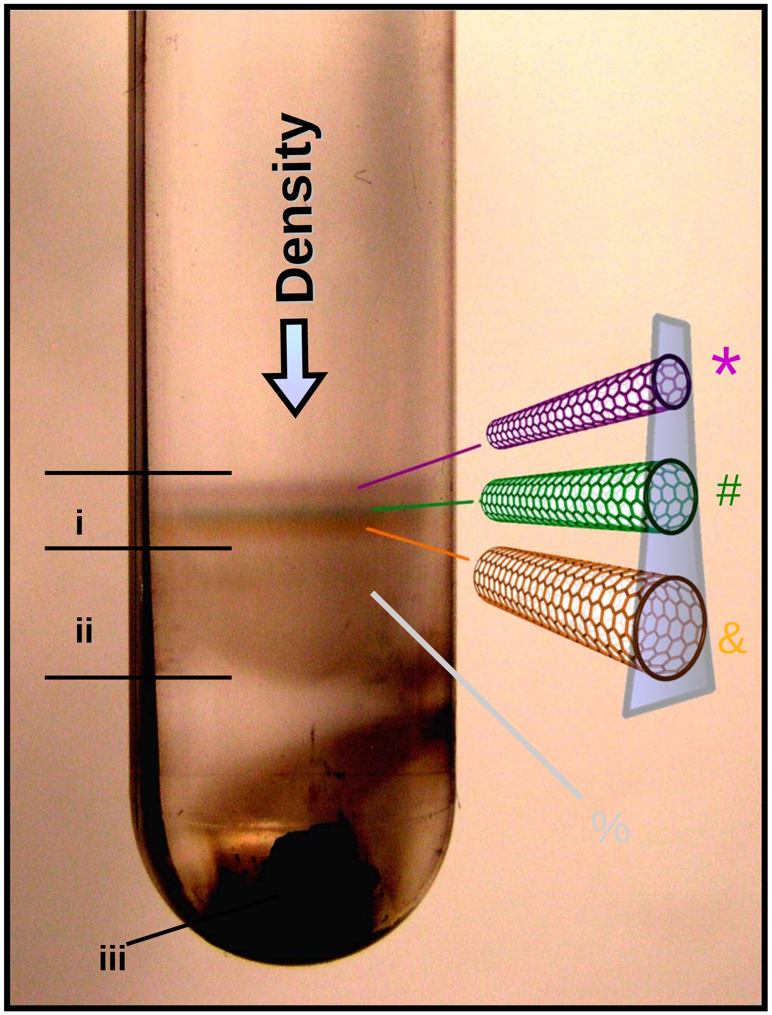
- Centrifugation at 174,000 *g* (64,000 rpm) for 10.5 hours.
- Density gradient formed using iodixanol and heavy water.
- DNA-wrapped nanotubes are stable in iodixinol.
- Initially, the SWNTs separate by sedimentation velocity.
- Then, as they approach their isopycnic point, they separate by density.
- The density gradient becomes steeper with time.



Resulting Separation

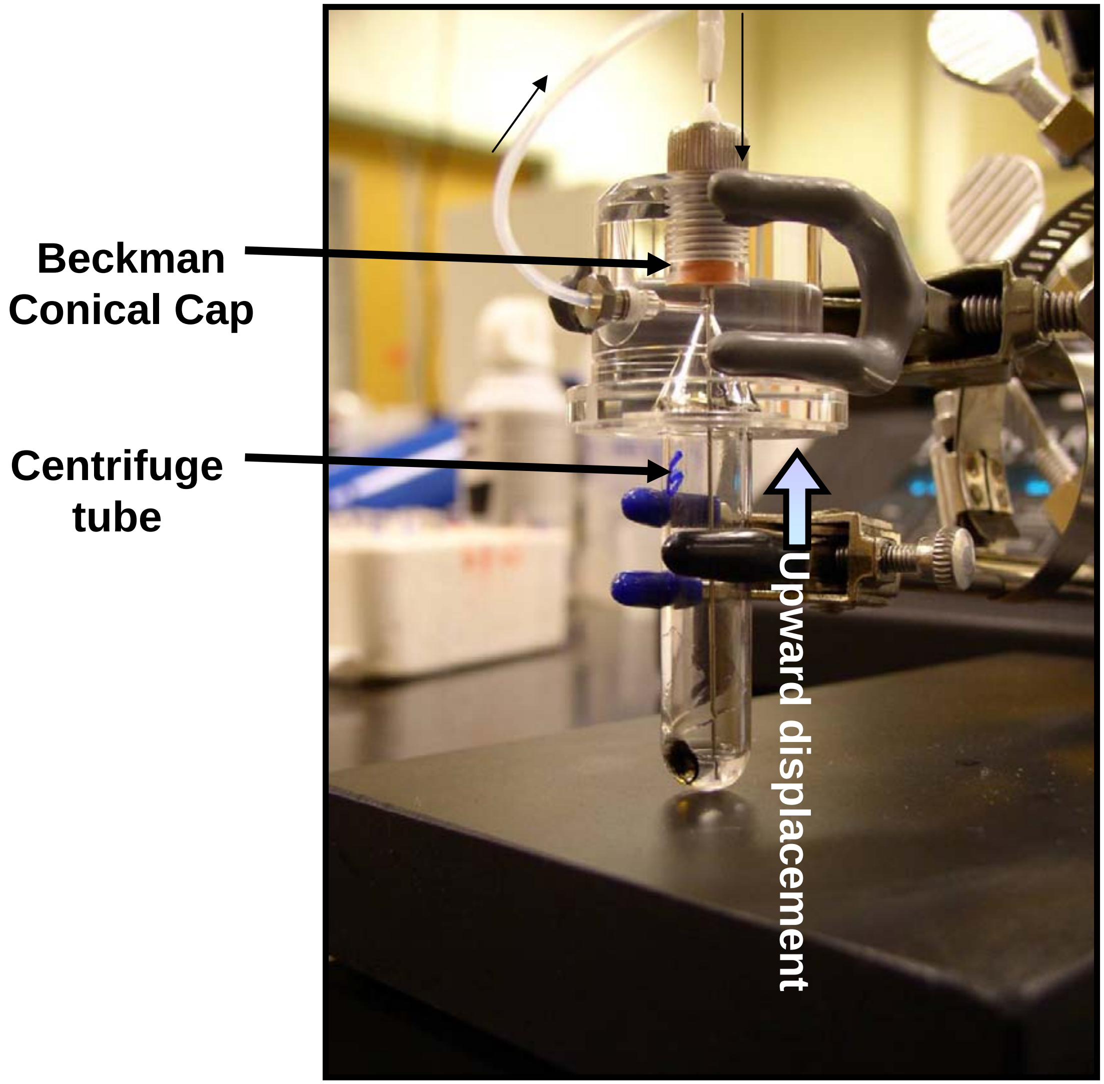
Nano Letters, **5**, 713 (2005).

- After 10.5 hours, the NTs have separated into three regions (i-iii).
- (i) Colored bands – isolated, fully functionalized nanotubes separated by physical and electronic structure (1.11-1.17 g cm^{-3})
- (ii) Grey colorless region – bundled or partially functionalized nanotubes / no separation by structure observed (> 1.17 g cm^{-3})
- (iii) Pellet – large aggregates and insoluble material



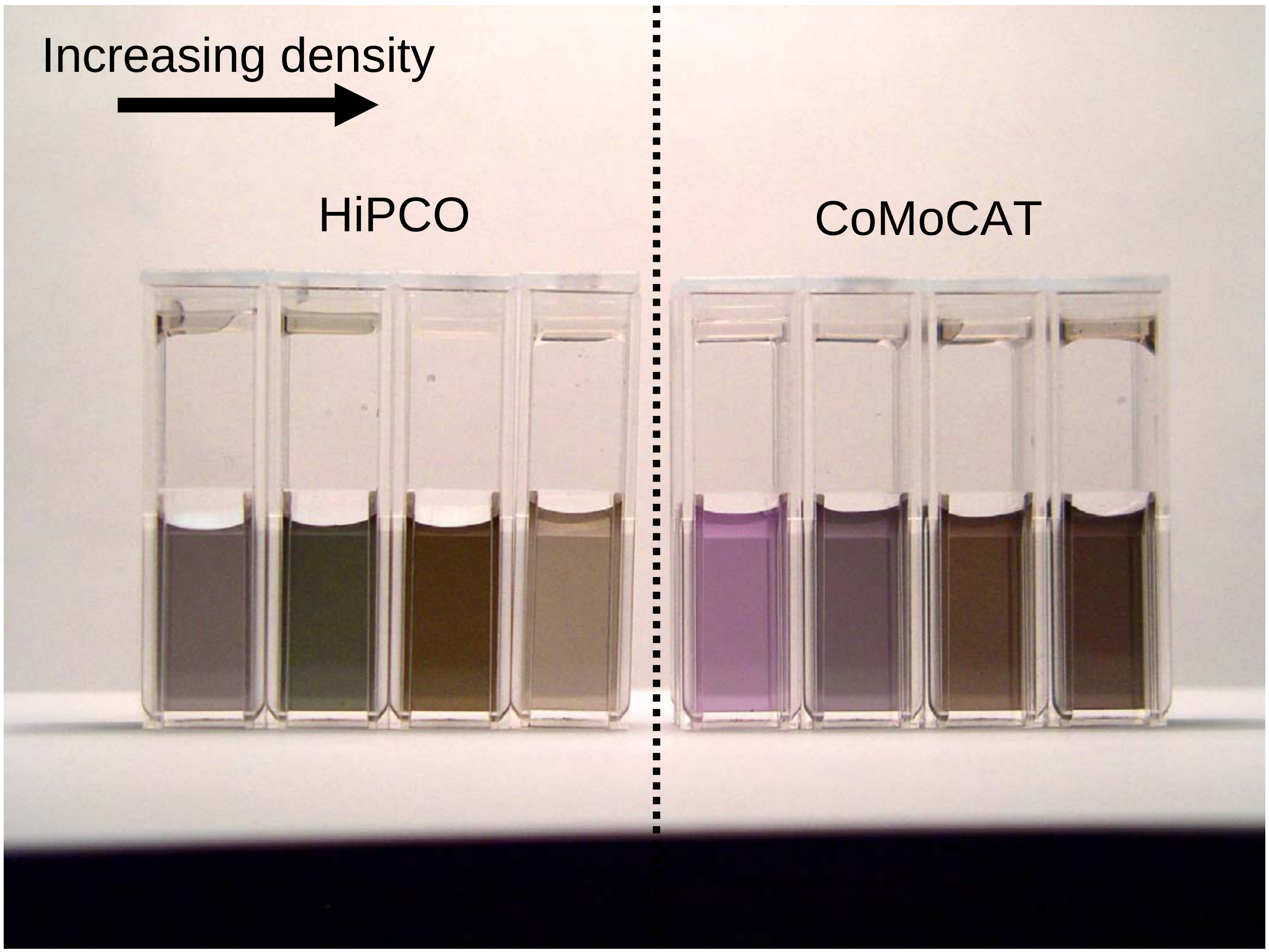
Fractionation

Nano Letters, **5**, 713 (2005).



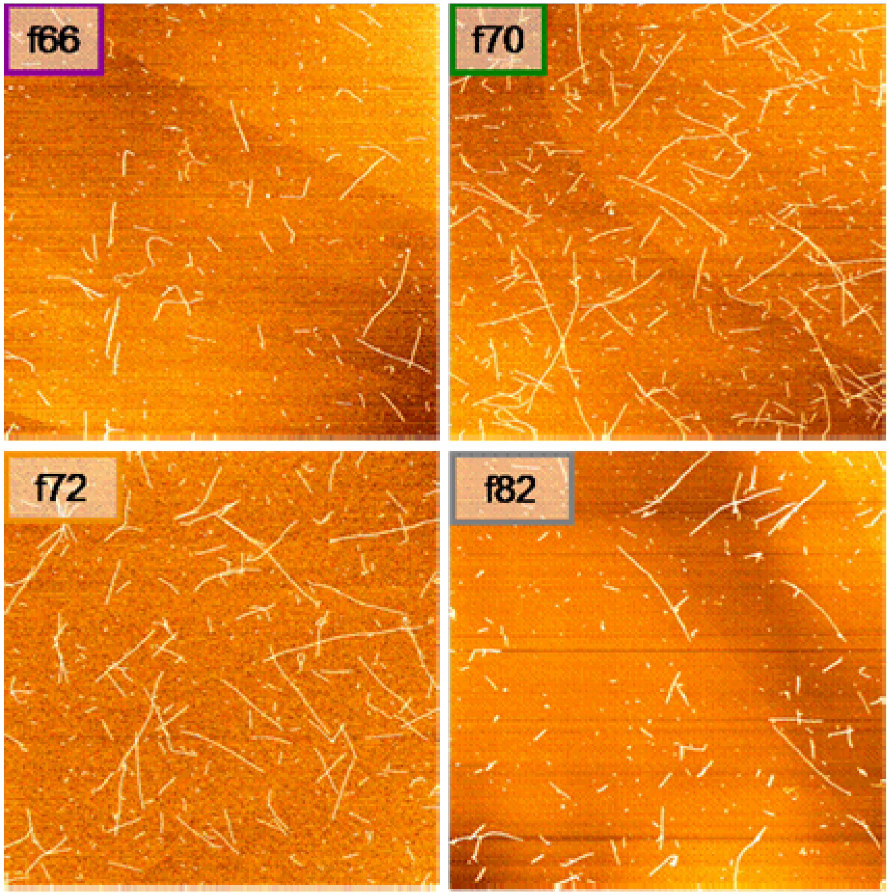
Resulting Fractions

Nano Letters, **5**, 713 (2005).

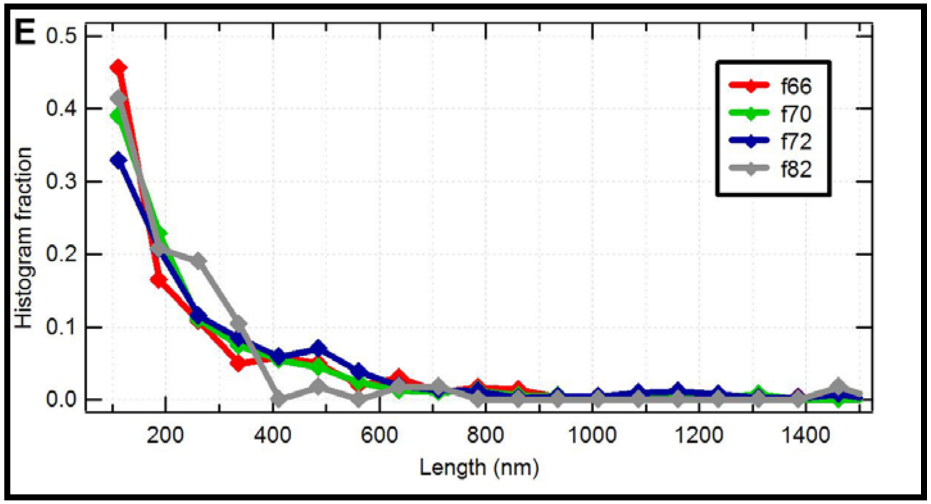


No Length Dependence

Nano Letters, **5**, 713 (2005).



all images, IC-AFM, (6 μm)^2



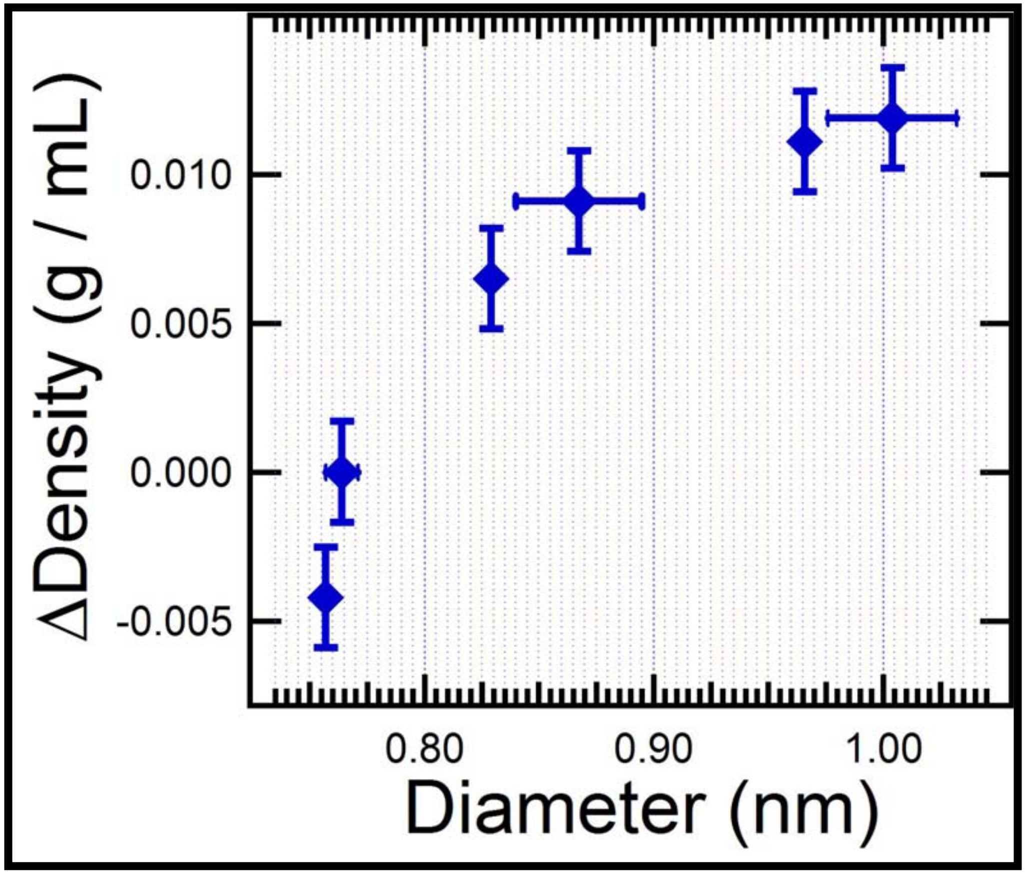
Similar length distributions were observed throughout regions i and ii (the colored bands and the grey region) of the density gradient.

Quantification of Separation by Diameter

Nano Letters, **5**, 713 (2005).

λ_{11s} (nm)	Chiralities	Diameters (Å)
929	(9, 1)	7.57
991	(6, 5), (8, 3)	7.57, 7.71
1040	(7, 5)	8.29
1134	(8, 4), (7, 6)	8.40, 8.95
1199	(8, 6)	9.66
1273	(9, 5), (8, 7)	9.76, 10.32

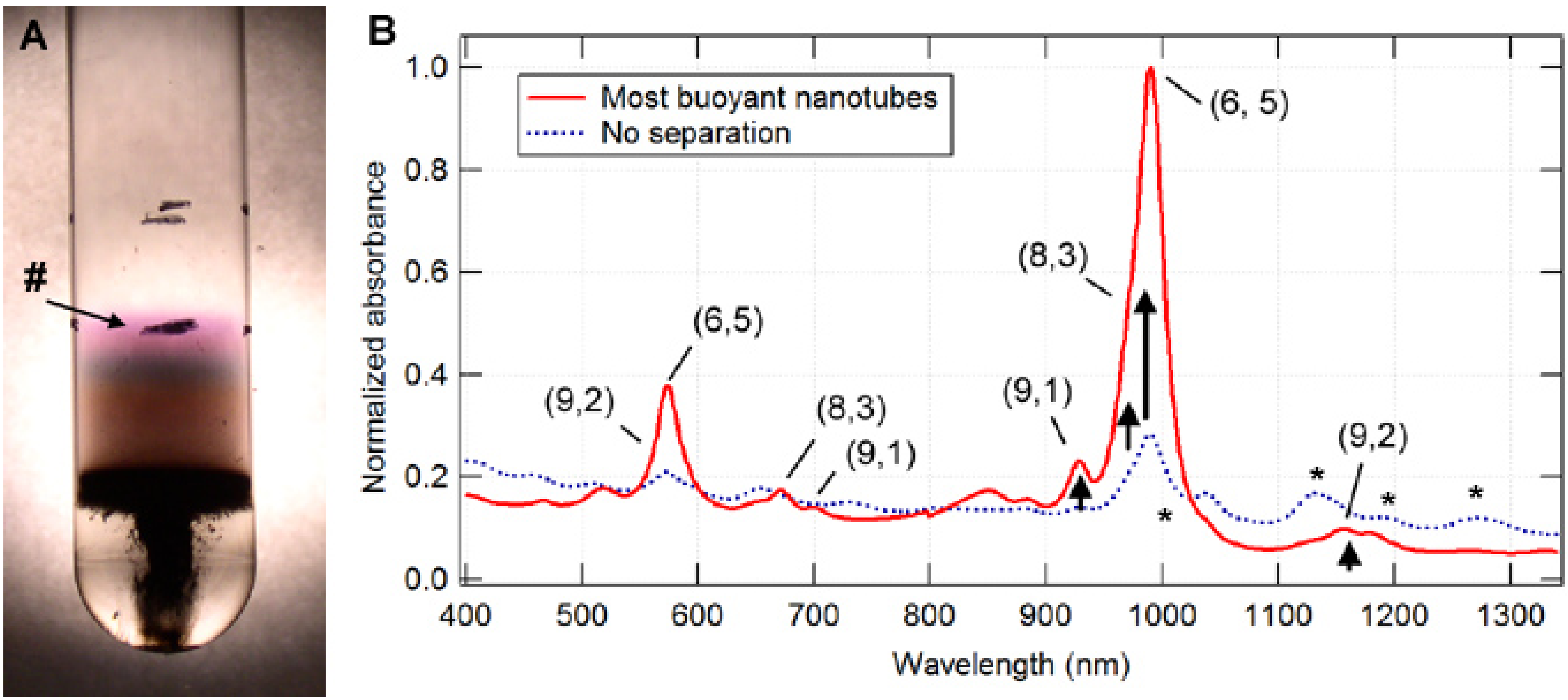
$$\rho_{NT} := \frac{\rho_s \pi D + \rho_{ext} \pi \left(\left(\frac{D}{2} + t \right)^2 - \frac{D^2}{4} \right)}{\pi \left(\frac{D}{2} + t \right)^2}$$



- Separation is most efficient for small SWNT diameters

Separation in a Shallow Gradient

Nano Letters, **5**, 713 (2005).



Spectra before (dotted blue line) and after (solid red line) selecting for CoMoCAT-grown SWNTs 7.6 Å in diameter using density gradient centrifugation.

Optical Properties of Chirality-Enriched SWNTs

Collaboration with Tobias Hertel (Vanderbilt Univ.) and Daniel Resasco (Univ. of Oklahoma)

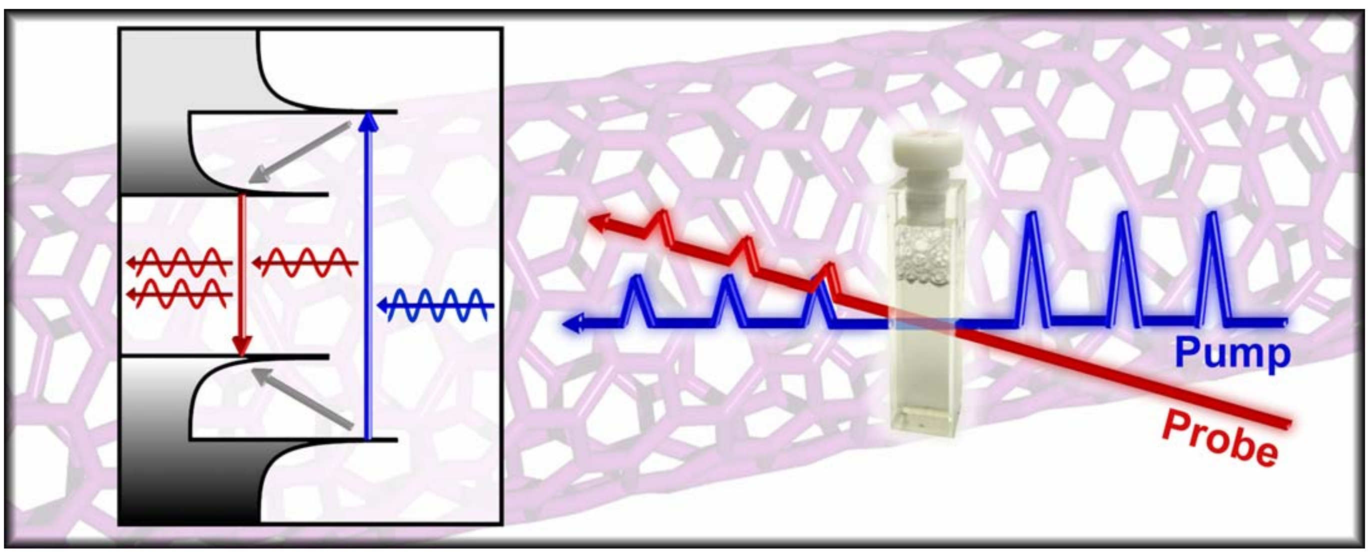
J. Phys. Chem. C **2007,** *111,* 3831−3835 **3831**

Pump-Probe Spectroscopy of Exciton Dynamics in (6,5) Carbon Nanotubes

Zipeng Zhu,[†] Jared Crochet,[†] Michael S. Arnold,[‡] Mark C. Hersam,[‡] Hendrik Ulbricht,[§] Daniel Resasco,[||] and Tobias Hertel*[,†,⊥]

Vanderbilt Institute of Nanoscale Science and Engineering, Department of Physics and Astronomy, Vanderbilt University, Nashville, Tennessee, Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois, Institute for Experimental Physics, University of Vienna, Vienna, Austria, and School of Chemical Engineering and Materials Science, University of Oklahoma, Norman, Oklahoma

Received: October 23, 2006; In Final Form: December 19, 2006



Desired Attributes of a SWNT Purification Process

How does density gradient centrifugation of DNA/SWNTs stand up to our criteria?

- Scalable (YES)
- Compatible with SWNTs of all lengths (YES) and diameters (**NO**)
- Utilizes non-covalent (YES) / reversible (**NO**) functionalization
- Iteratively repeatable (**NO**)
- Economical (**NO**)

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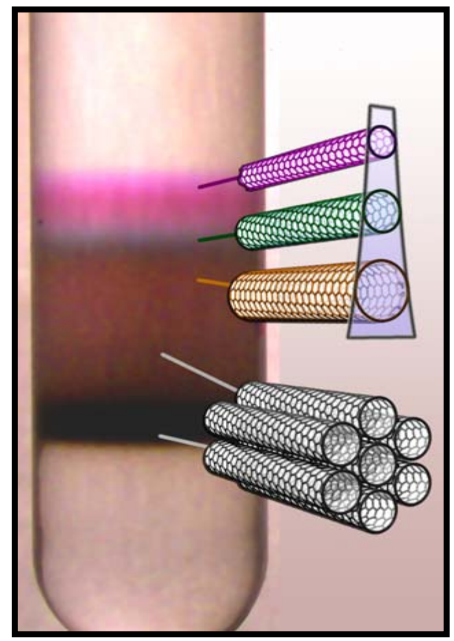
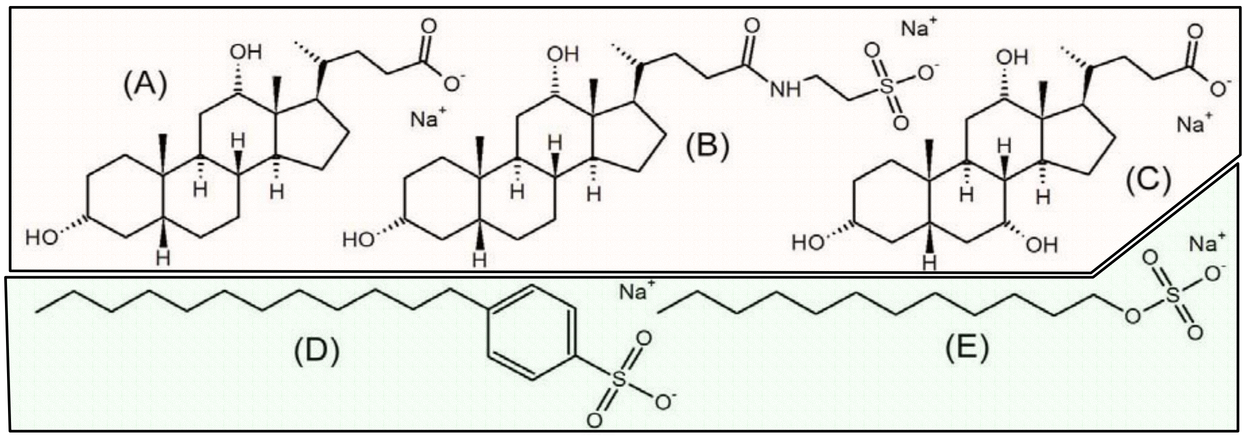
- Applications and commercialization



Surfactants

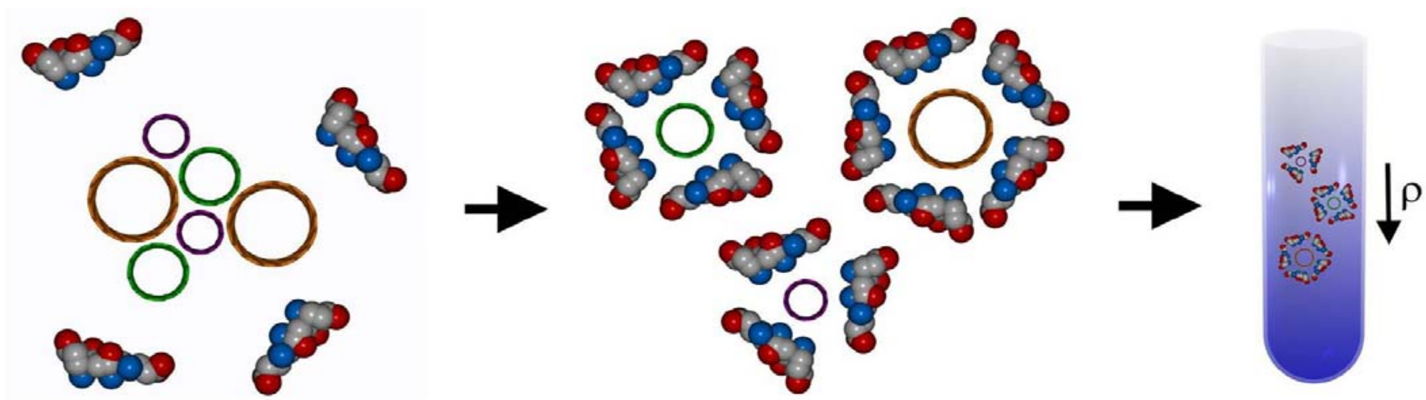
Nature Nanotechnology, **1**, 60 (2006).



Bile salts

Traditional head-to-tail surfactants

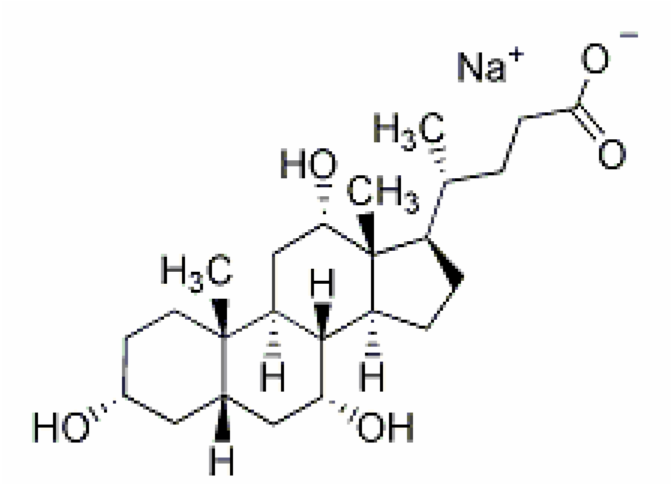
(A) Sodium deoxycholate **(B)** sodium taurodeoxycholate **(C)** sodium cholate
(D) sodium dodecylbenzene sulfonate (SDDBS) **(E)** sodium dodecyl sulfate (SDS)



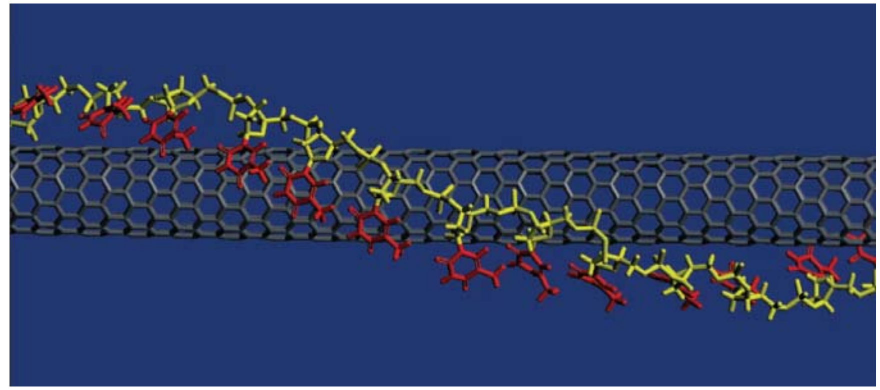
Dispersion and density gradient centrifugation of sodium cholate encapsulated SWNTs of various diameters

Sodium Cholate versus DNA

Nature Nanotechnology, **1**, 60 (2006).



Sodium cholate



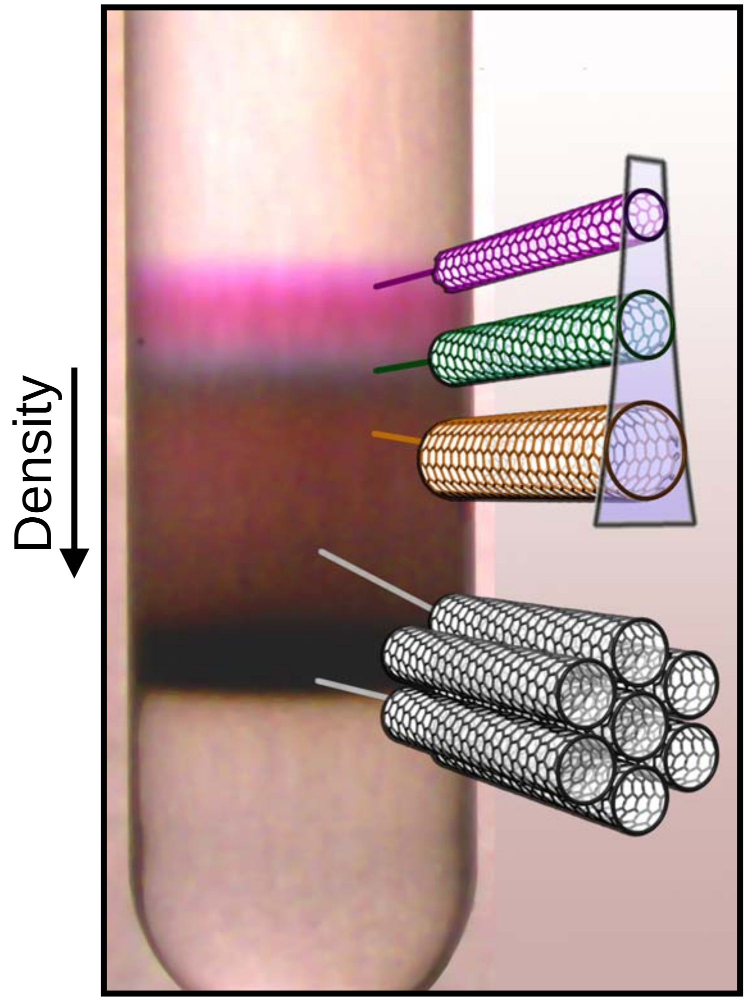
Single-stranded DNA

• $0.62/g (100 g scale) ---------------- • $2242.80/g (largest offered, 150 mg scale)

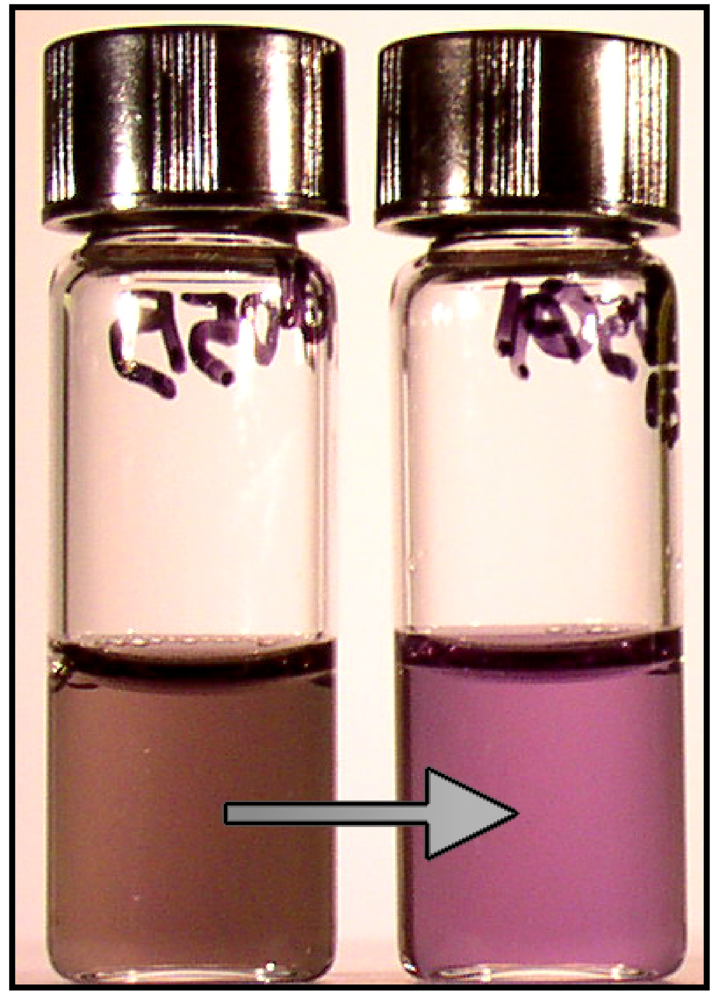
• Reversible encapsulatation --------- • Irreversible wrapping?

• Can solubilize nanotubes of various diameters --------- • Most efficiently wraps SWNTs near 0.7-1.0 nm in diameter

Density Gradient Centrifugation with Sodium Cholate



Sodium cholate encapsulated SWNTs after density gradient centrifugation



Initial material and isolated of the purple layer (dominated by the (6, 5) chirality)

Resulting Fractions

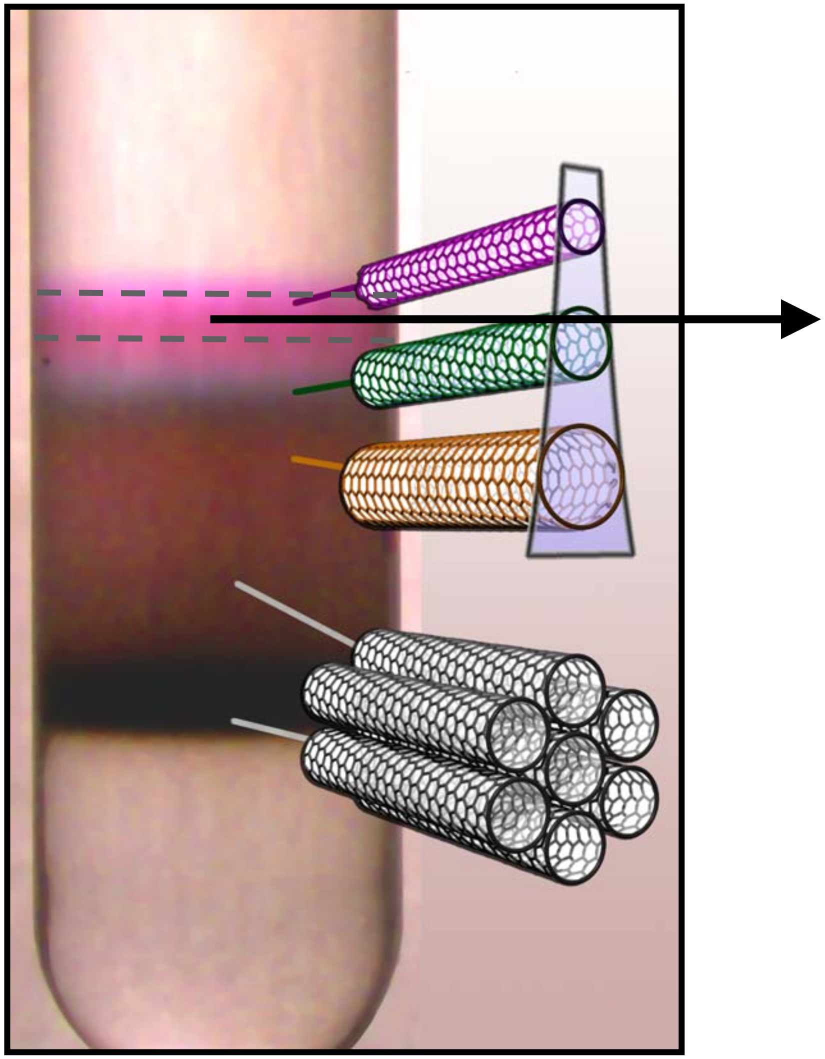
Nature Nanotechnology, **1**, 60 (2006).

A wide range of optically pure SWNT samples can be produced in one density gradient centrifugation step

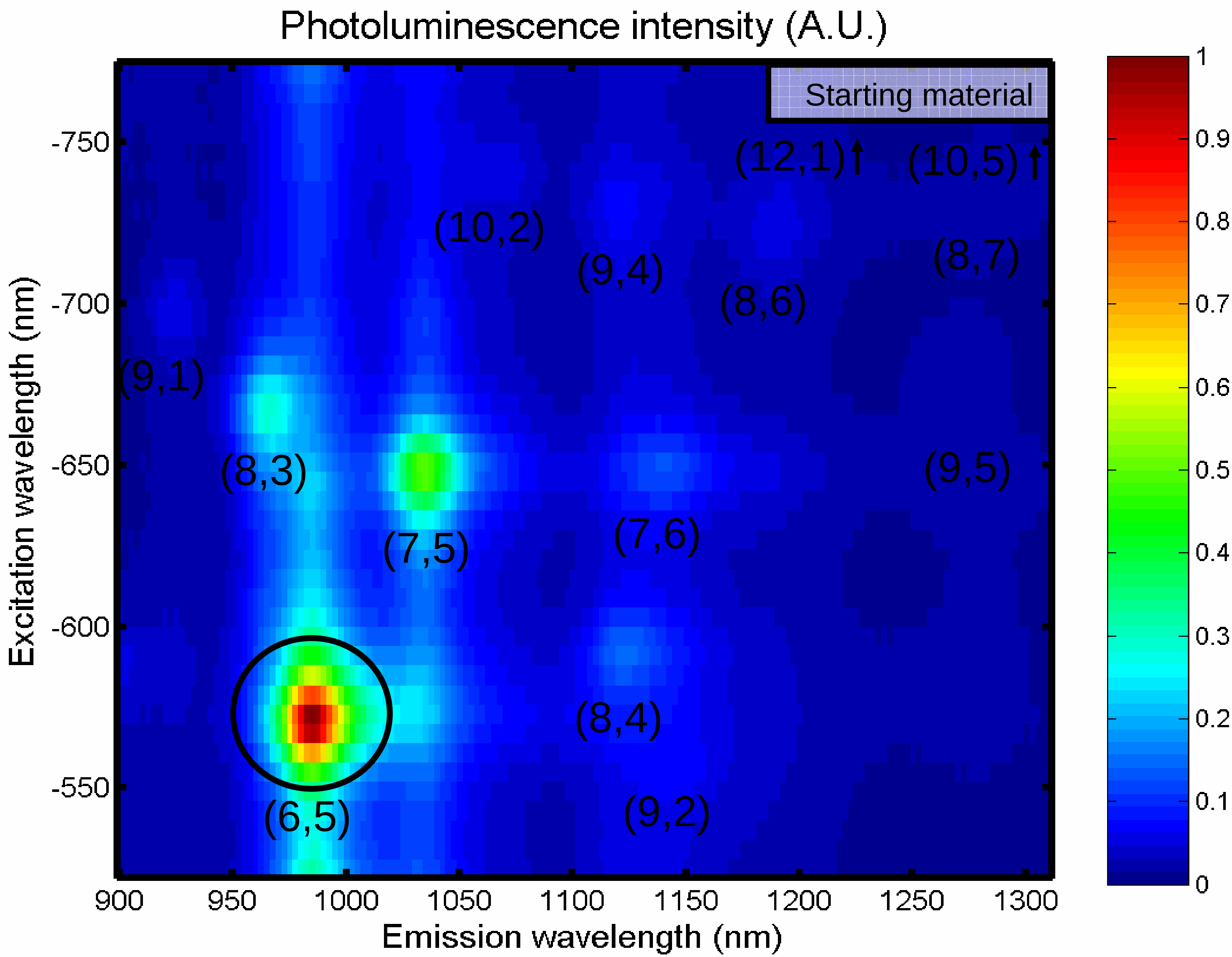
(Raw material = HiPCO SWNTs)

Multiple Iterations of Purification

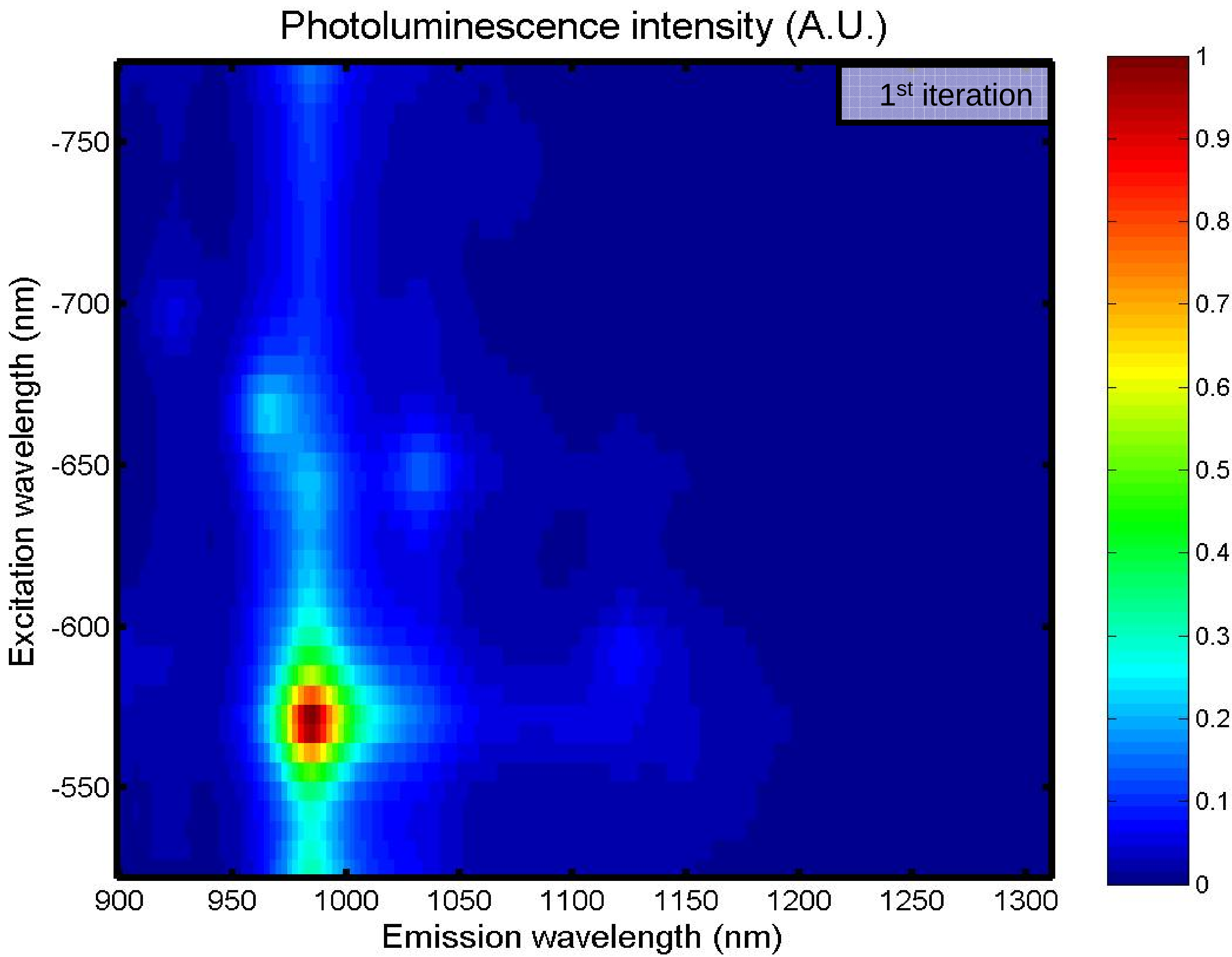
Nature Nanotechnology, **1**, 60 (2006).



- Remove a fraction (in which the concentration of the target chirality is maximized)
- Re-run it in a 2nd gradient
- Repeat



Photoluminescence intensity (A.U.)
Starting material
(12,1)
(10,5)
(10,2)
(9,4)
(8,6)
(8,7)
(9,1)
(8,3)
(7,5)
(7,6)
(9,5)
(8,4)
(6,5)
(9,2)
-750
-700
-650
-600
-550
900
950
1000
1050
1100
1150
1200
1250
1300
Emission wavelength (nm)
Excitation wavelength (nm)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0


Photoluminescence intensity (A.U.)
1st iteration
Excitation wavelength (nm)
-750
-700
-650
-600
-550
900
950
1000
1050
1100
1150
1200
1250
1300
Emission wavelength (nm)
1
0.9
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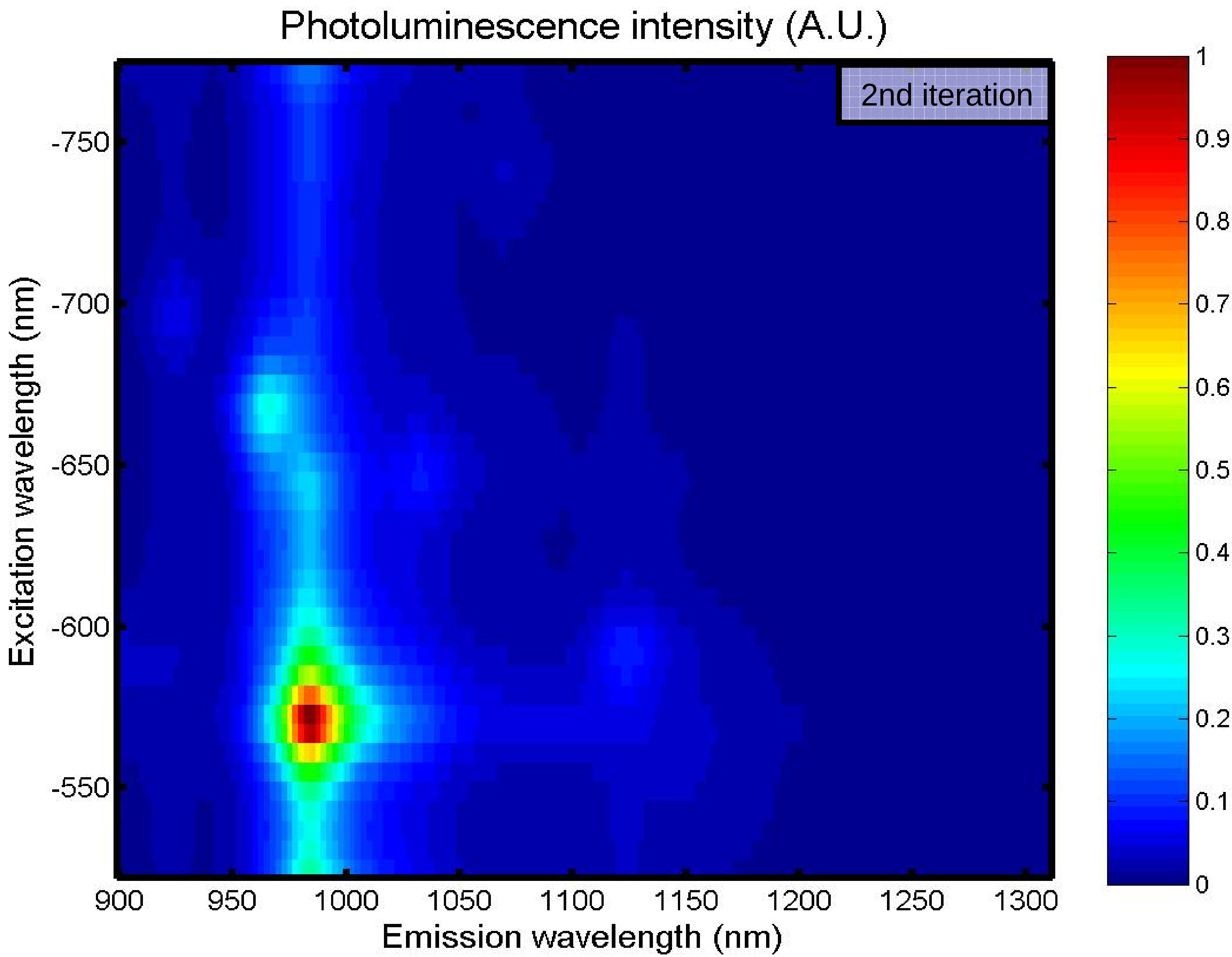
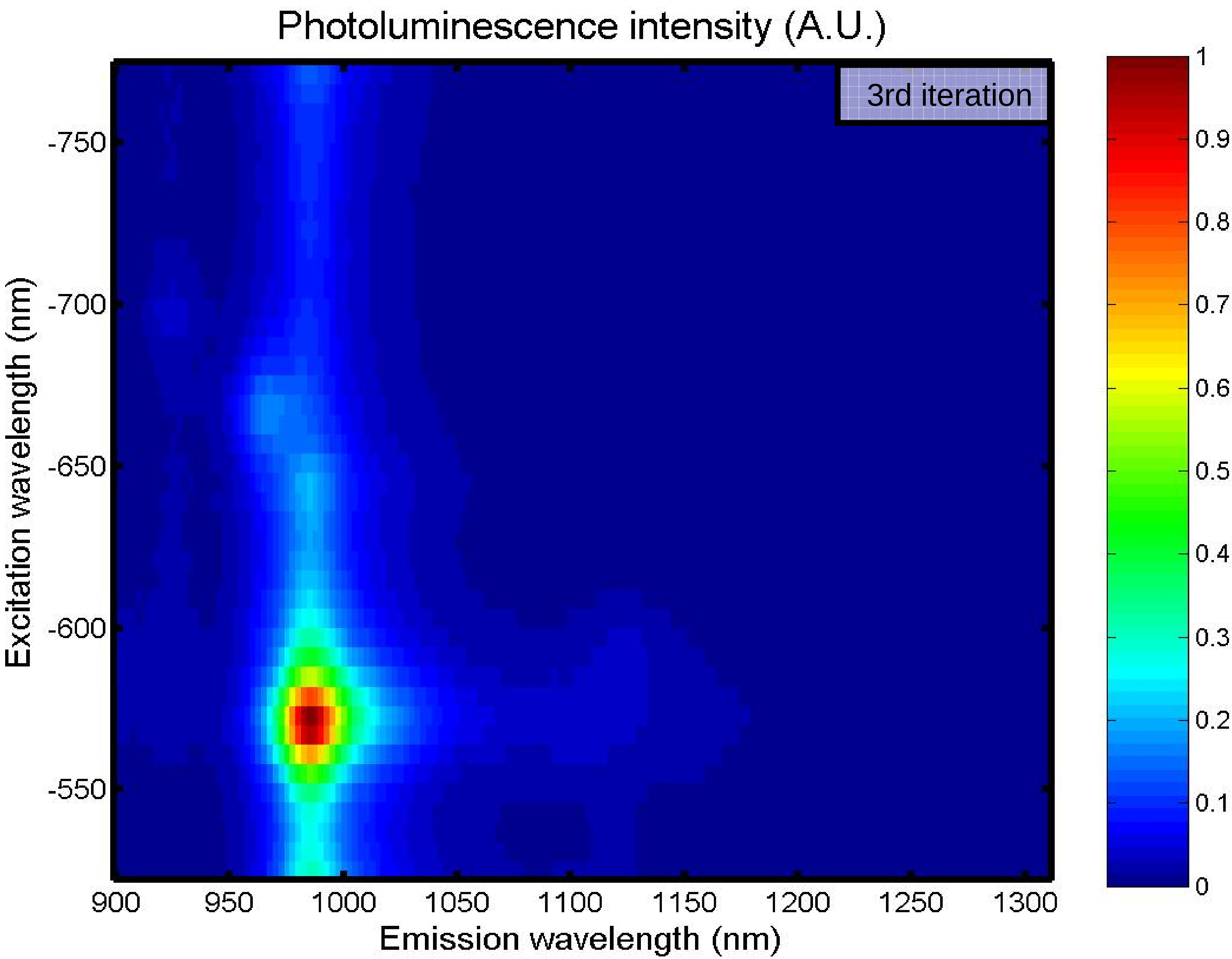
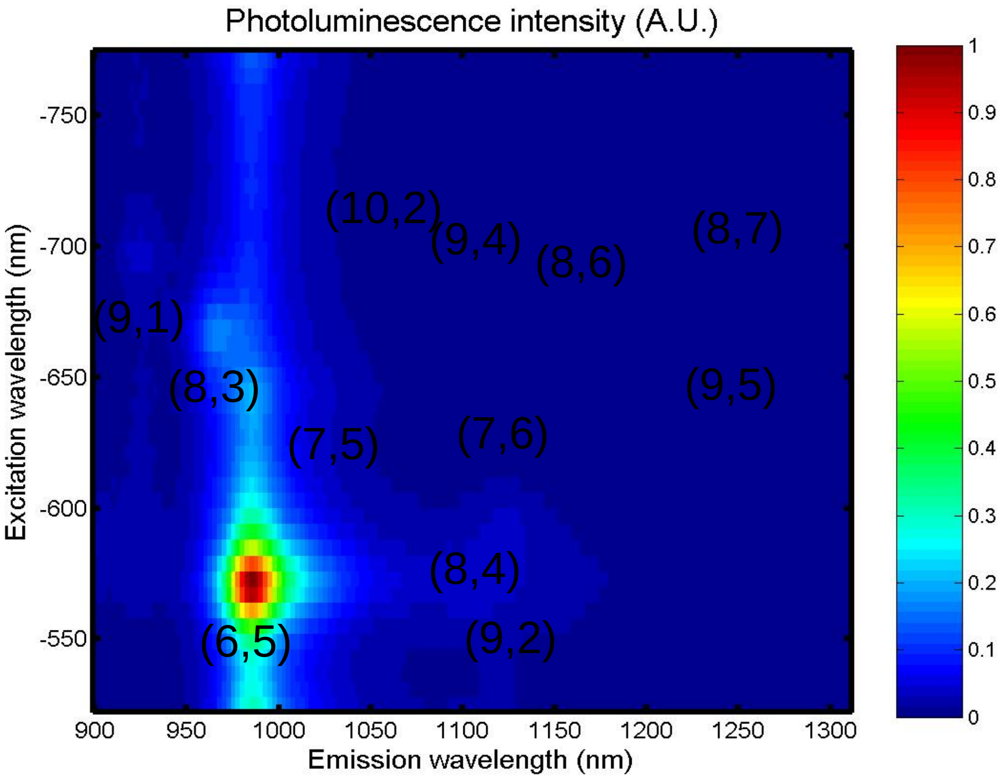
0.2
0.1
0



Photoluminescence intensity (A.U.)
2nd iteration
Excitation wavelength (nm)
-750
-700
-650
-600
-550
Emission wavelength (nm)
900
950
1000
1050
1100
1150
1200
1250
1300
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0

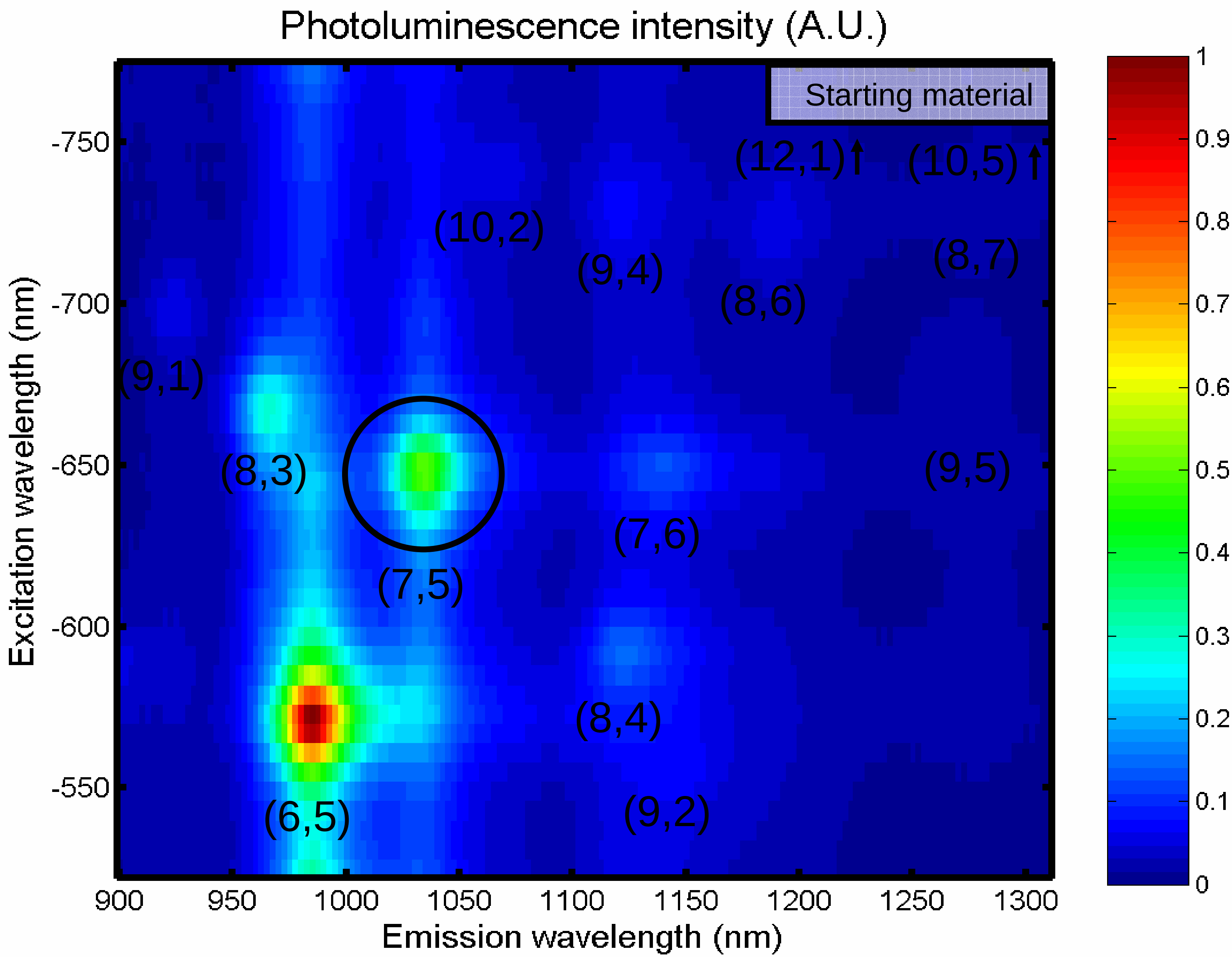

Photoluminescence intensity (A.U.)
3rd iteration
-750
-700
-650
-600
-550
Excitation wavelength (nm)
900
950
1000
1050
1100
1150
1200
1250
1300
Emission wavelength (nm)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0

> 97% within 0.02 nm of mean diameter



Chirality	Diameter (Å)	Initial	(6, 5) purf.
(6, 5)	7.57	45.41%	83.64%
(9, 1)	7.57	1.92%	2.39%
(8, 3)	7.82	11.46%	11.04%
(9, 2)	8.05	1.00%	0.04%
(7, 5)	8.28	23.01%	0.66%
(8, 4)	8.40	5.02%	1.48%
(10, 2)	8.84	1.78%	0.61%
(7, 6)	8.94	4.34%	0.08%
(9, 4)	9.15	2.55%	0.00%
(8, 6)	9.65	2.33%	0.00%
(9, 5)	9.75	0.32%	0.03%
(8, 7)	10.32	0.86%	0.04%

Mean = 0.76 nm



Photoluminescence intensity (A.U.)
Starting material
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(10,2)
(9,4)
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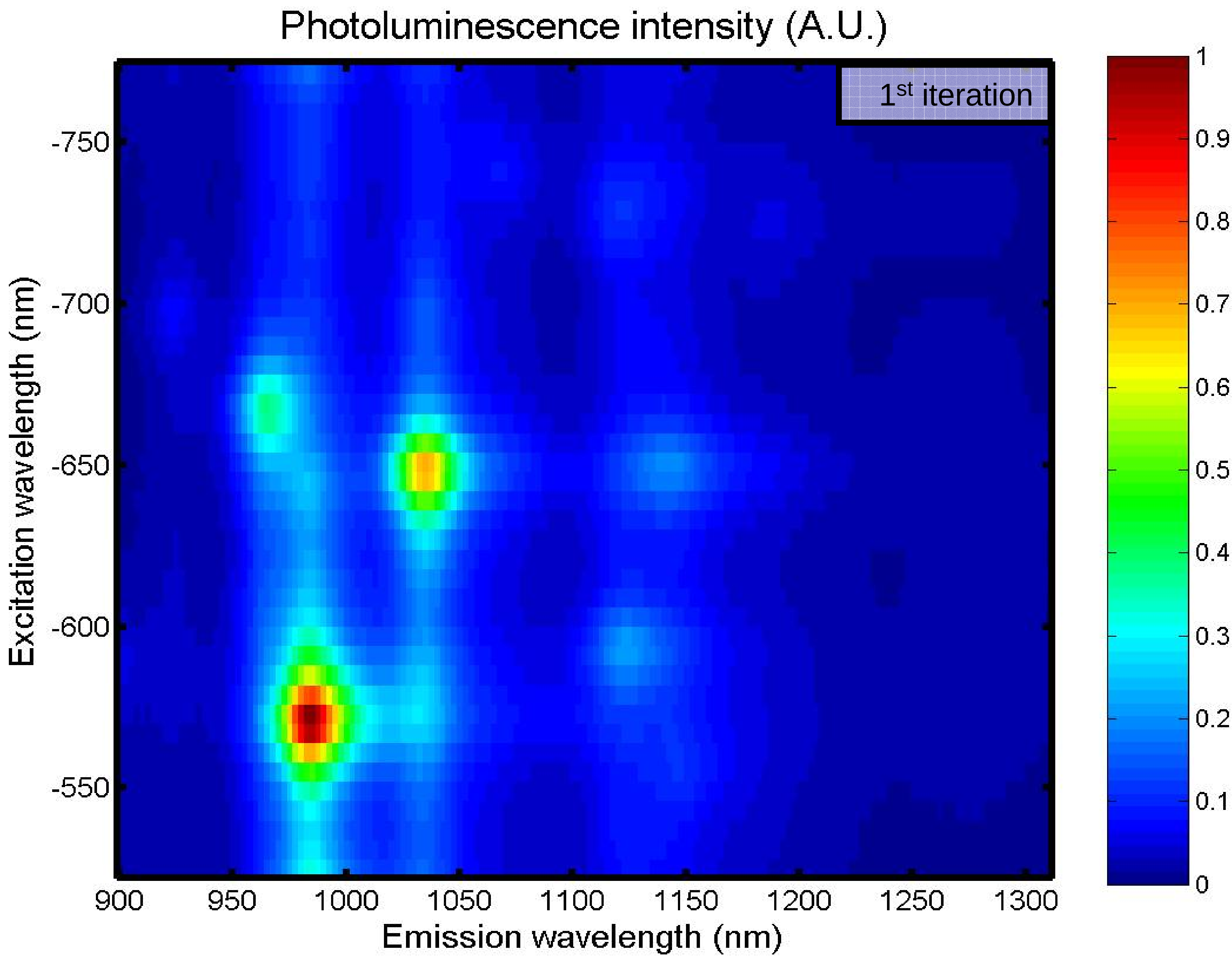
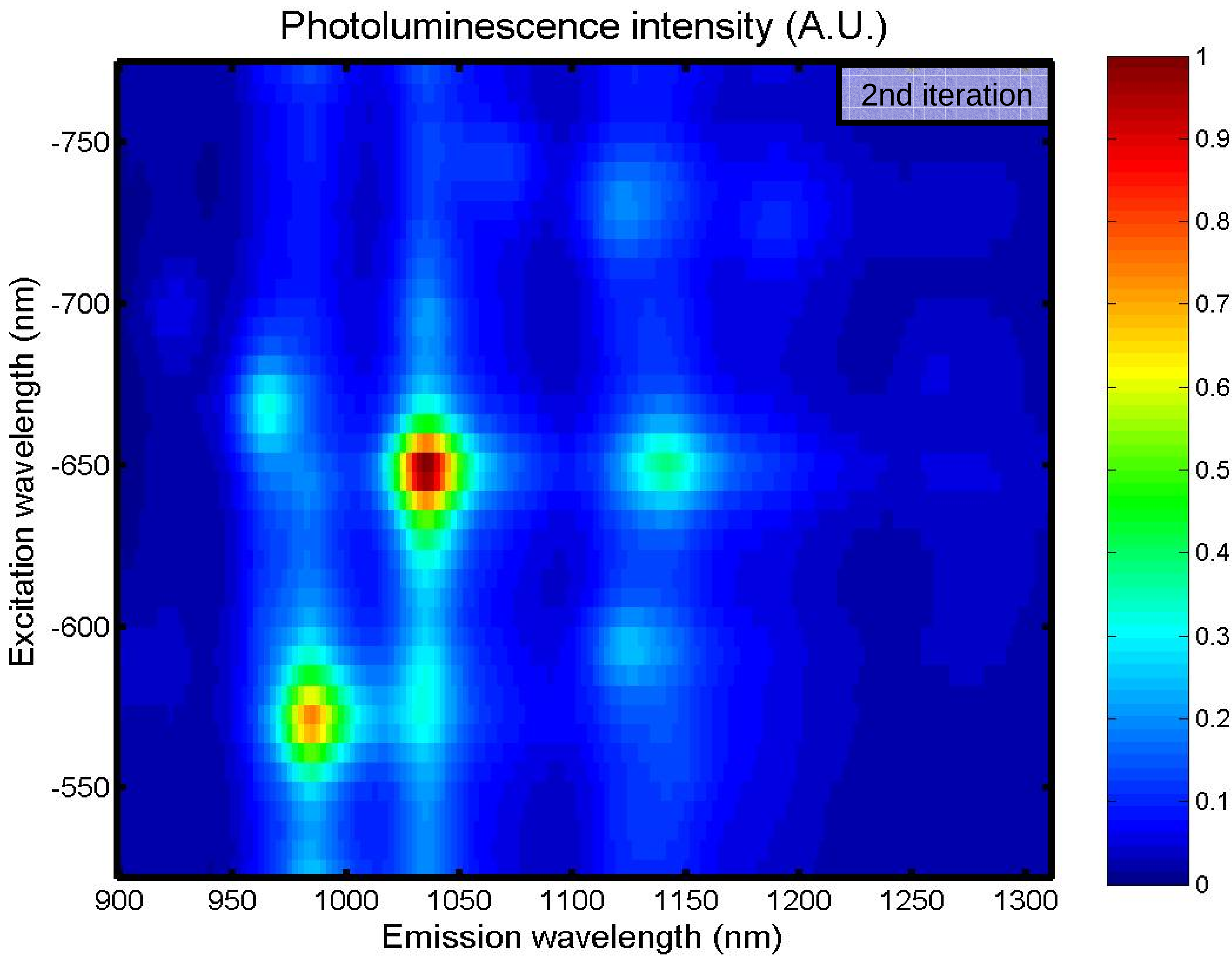
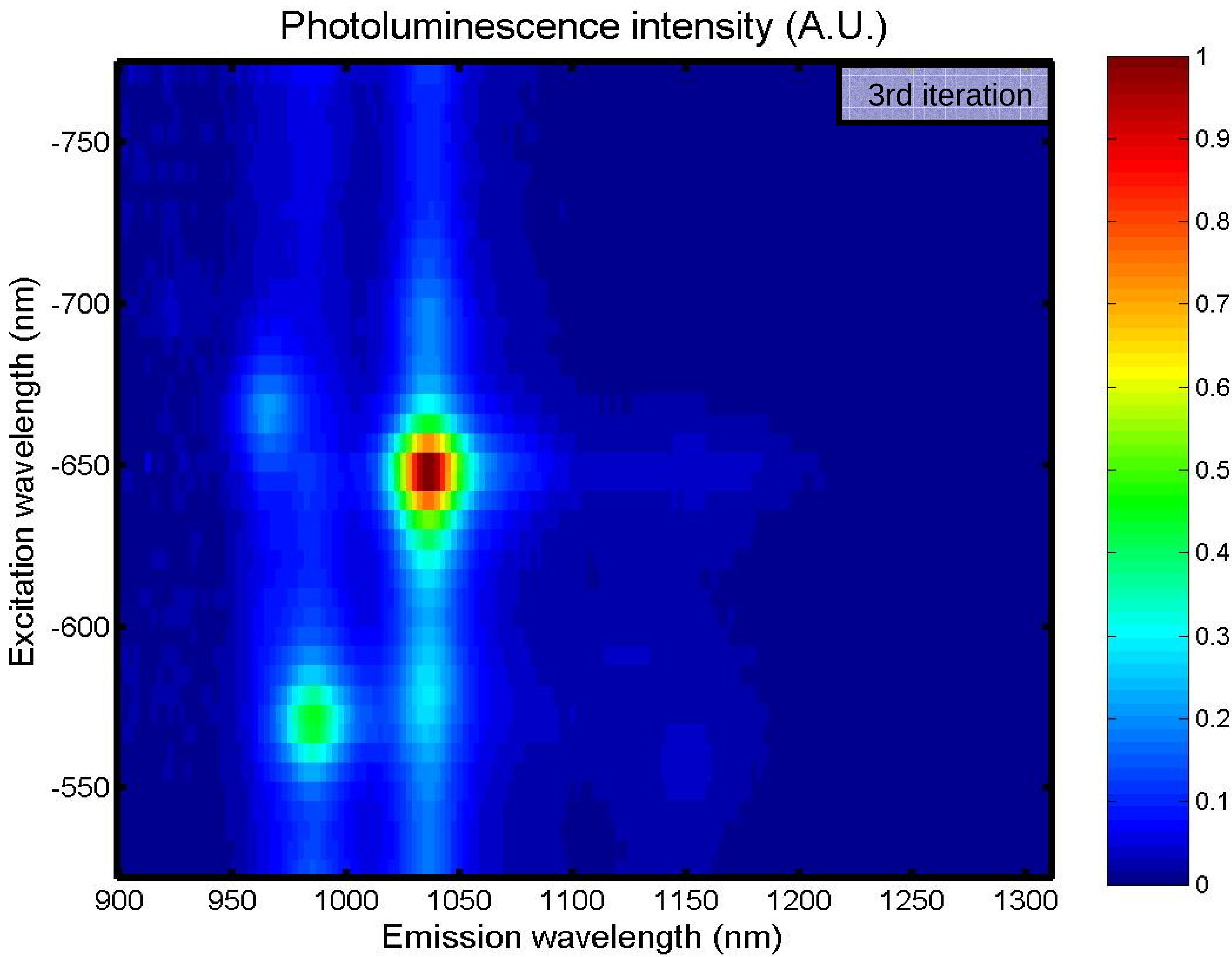
1250
1300
Emission wavelength (nm)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0


Photoluminescence intensity (A.U.)
1st iteration
Excitation wavelength (nm)
-750
-700
-650
-600
-550
Emission wavelength (nm)
900
950
1000
1050
1100
1150
1200
1250
1300
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0



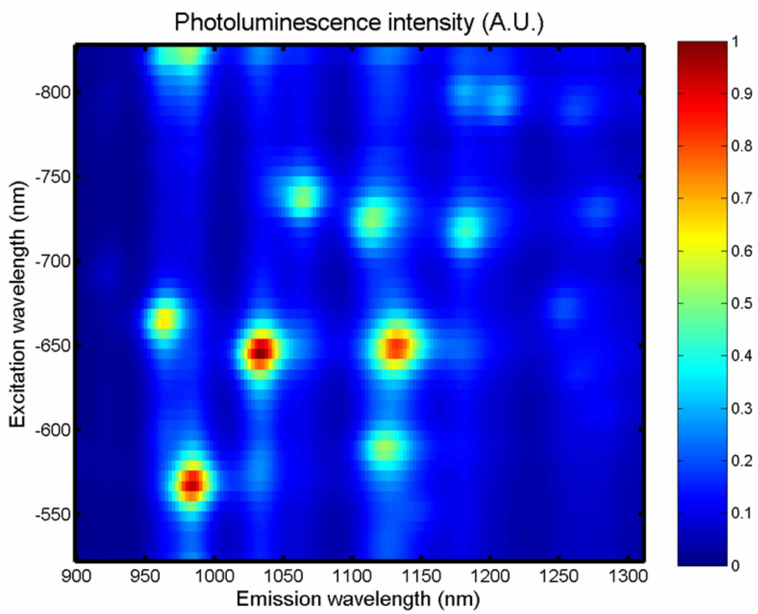
Photoluminescence intensity (A.U.)
2nd iteration
Excitation wavelength (nm)
-750
-700
-650
-600
-550
900
950
1000
1050
1100
1150
1200
1250
1300
Emission wavelength (nm)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0


Photoluminescence intensity (A.U.)
3rd iteration
-750
-700
-650
-600
-550
Excitation wavelength (nm)
900
950
1000
1050
1100
1150
1200
1250
1300
Emission wavelength (nm)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0

Diameter Tunability with Co-Surfactants

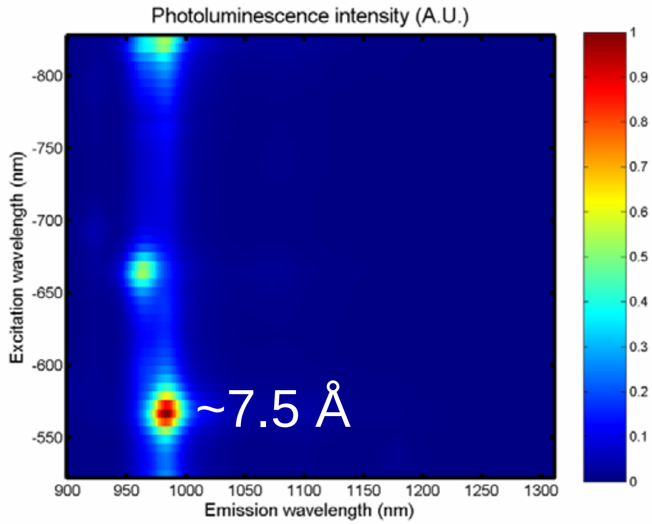
Nature Nanotechnology, **1**, 60 (2006).

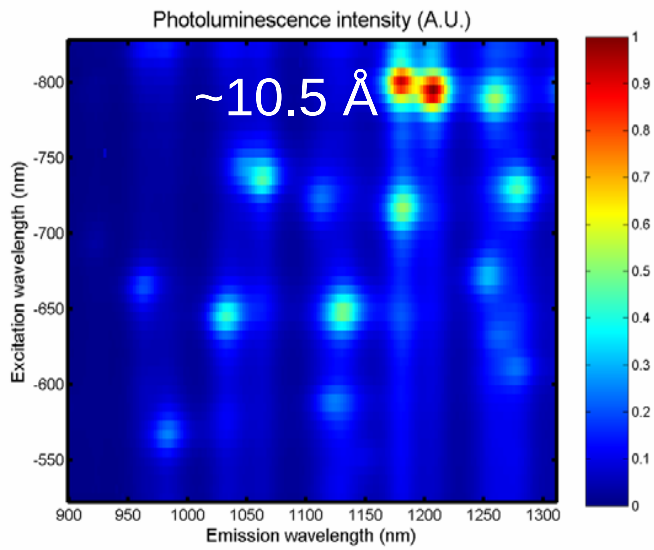
3 parts sodium dodecyl sulfate,
7 parts sodium cholate



Smaller diameters

Larger diameters





Purification of Large Diameter SWNTs

Collaboration with Phaedon Avouris (IBM)

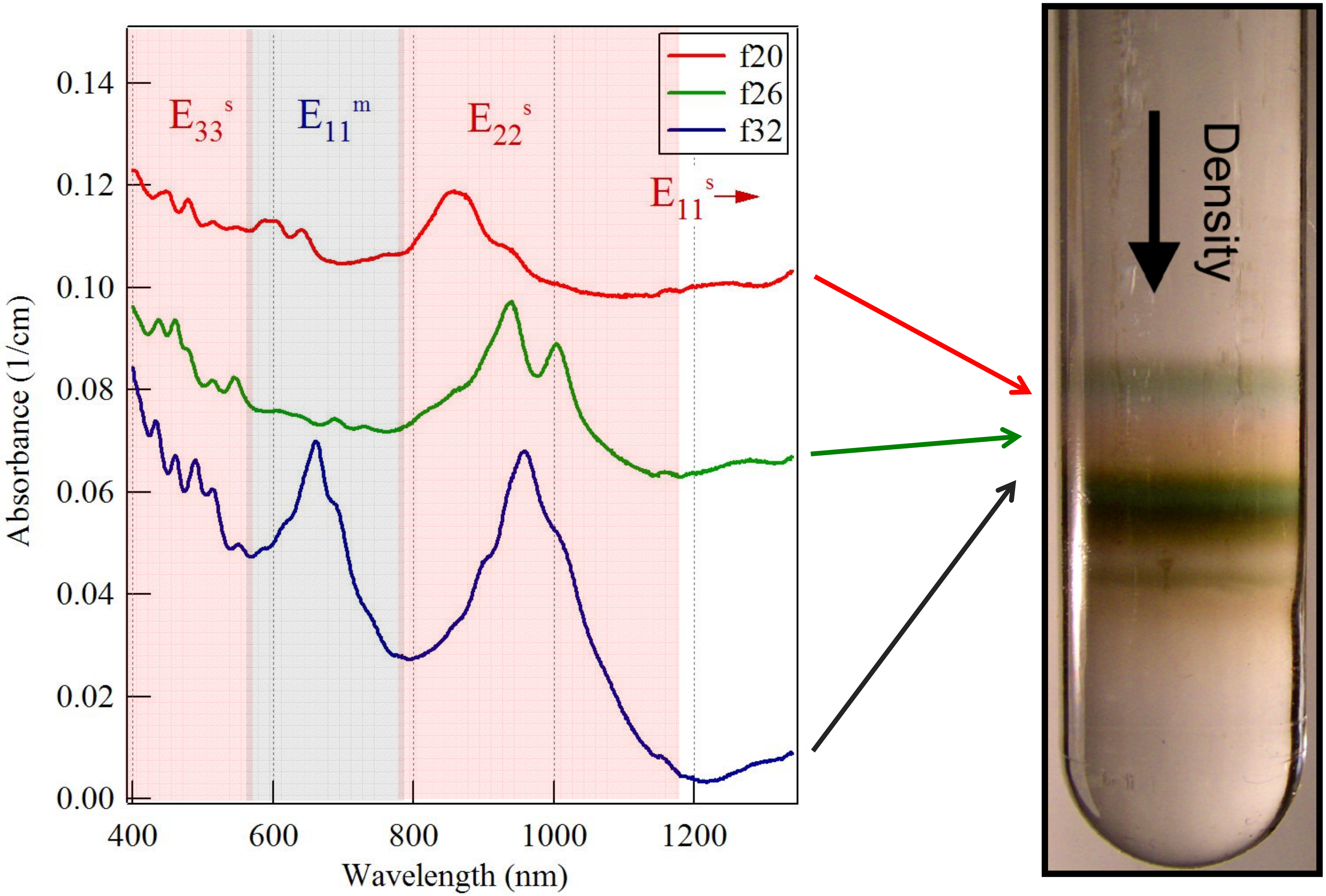
- CoMoCAT-grown and HiPCO-grown SWNTs (7-11 Å) are possibly too small for electronics (large Schottky barrier).
- Can we separate tubes in the 11-16 Å range (laser-ablation)?

YES

Sodium cholate encapsulated SWNTs grown by the laser ablation method after separation in a density gradient

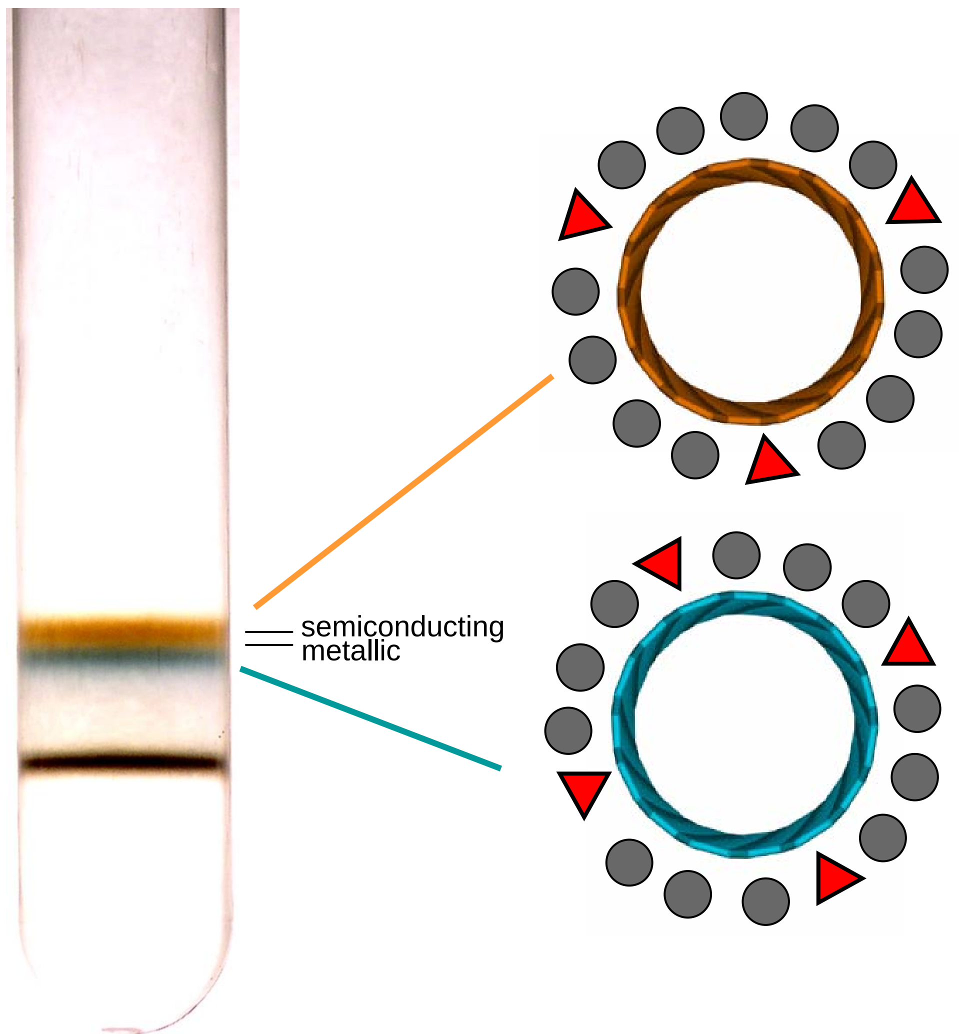
Purification by Diameter and Electronic Type

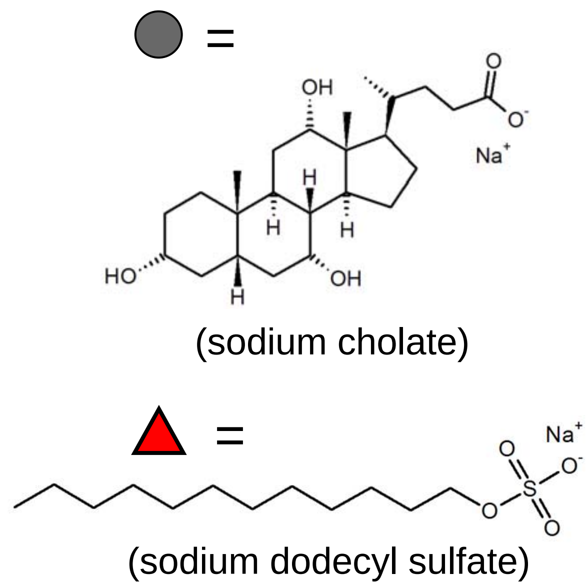
Nature Nanotechnology, **1**, 60 (2006).



Electronic Type Sensitivity with Co-Surfactants

Nature Nanotechnology, **1**, 60 (2006).

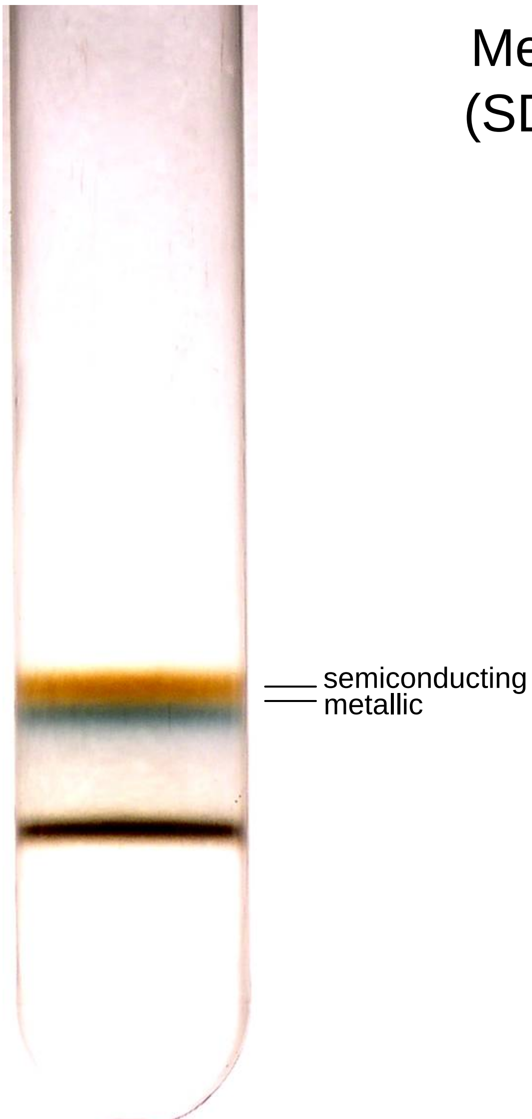


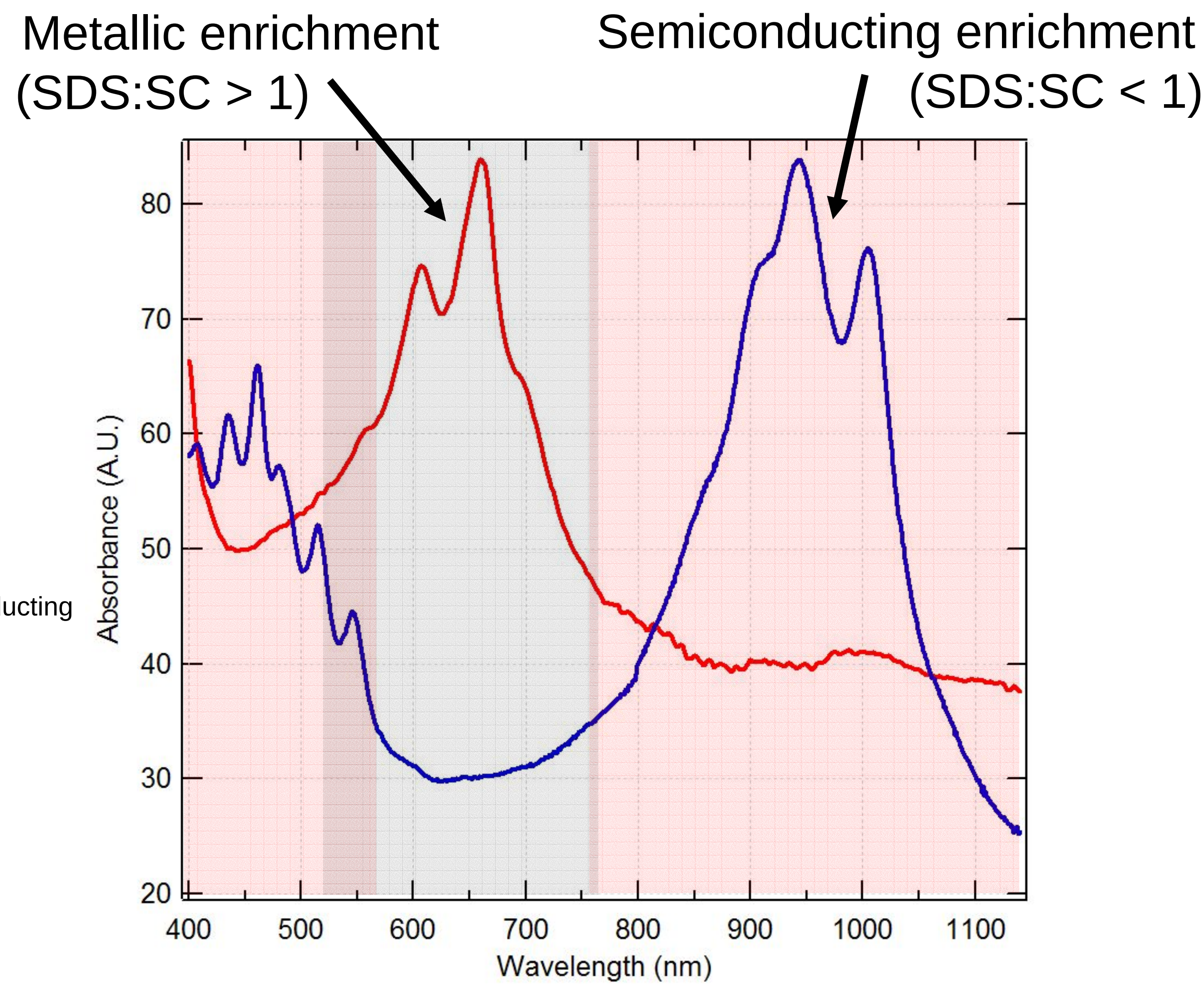


<u>Hypothesis</u>: Different surfactants have slightly different affinities toward one electronic-type

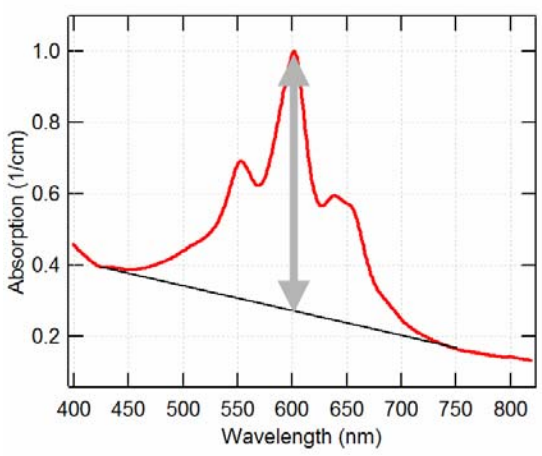
Metal versus Semiconductor Separation

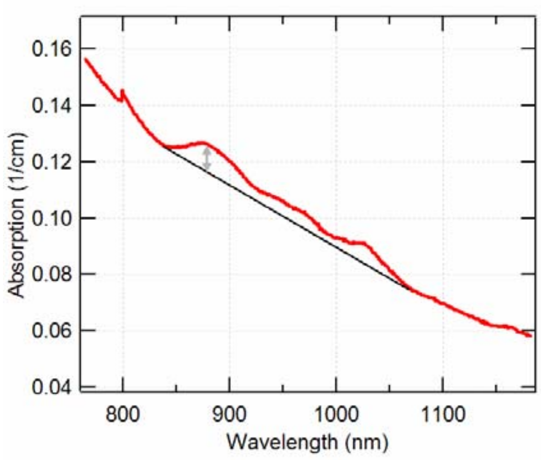
Nature Nanotechnology, **1**, 60 (2006).





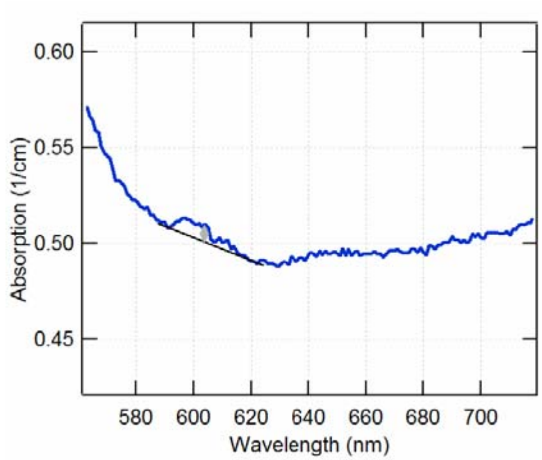
Quantification of Electronic Type Separation

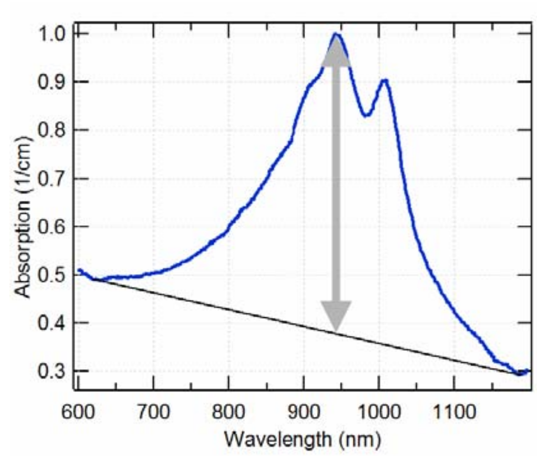




Analysis of optical absorption spectrum

~99.3% metallic





Analysis of optical absorption spectrum

~97.5% semiconducting

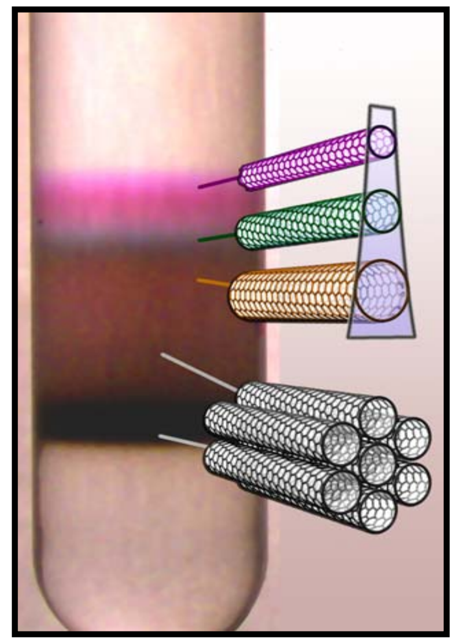
Desired Attributes of a SWNT Purification Process

How does density gradient centrifugation of surfactant/SWNTs stand up to our criteria?

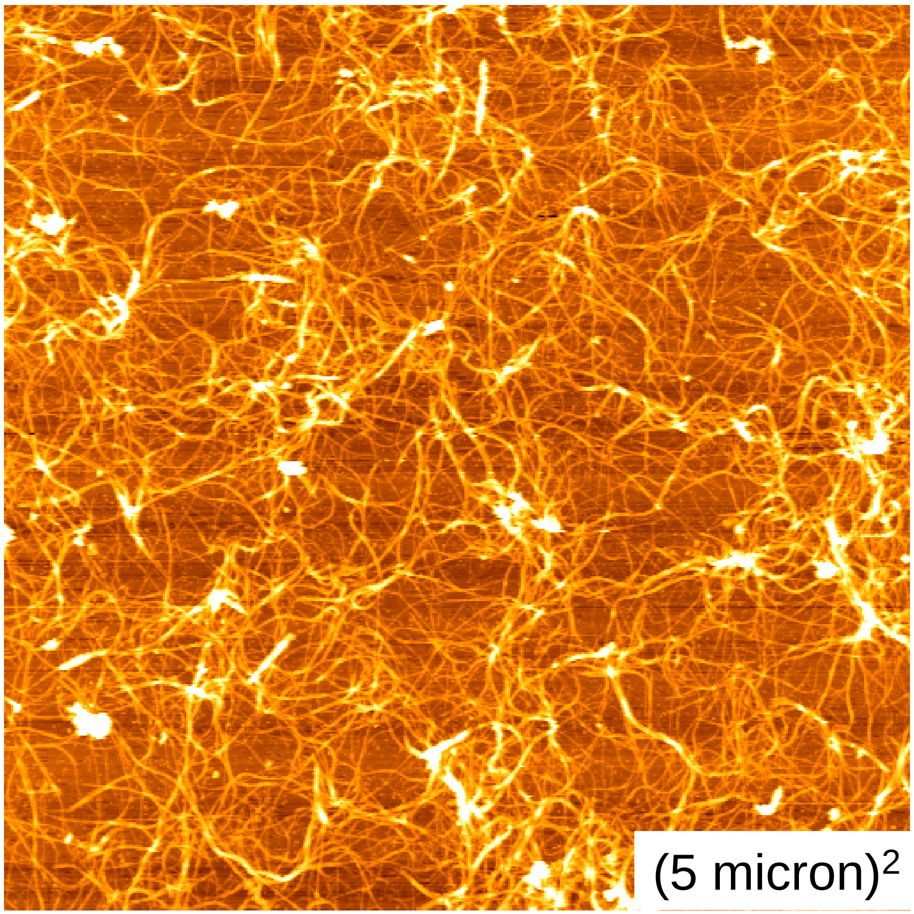
- Scalable (YES)
- Compatible with SWNTs of all lengths (YES) and diameters (YES)
- Utilizes non-covalent (YES) / reversible (YES) functionalization
- Iteratively repeatable (YES)
- Economical (YES)

Outline

- Motivation and background information
- Density gradient centrifugation of DNA encapsulated SWNTs
- Density gradient centrifugation of surfactant encapsulated SWNTs
- Applications and commercialization



Possible Applications for Purified SWNTs

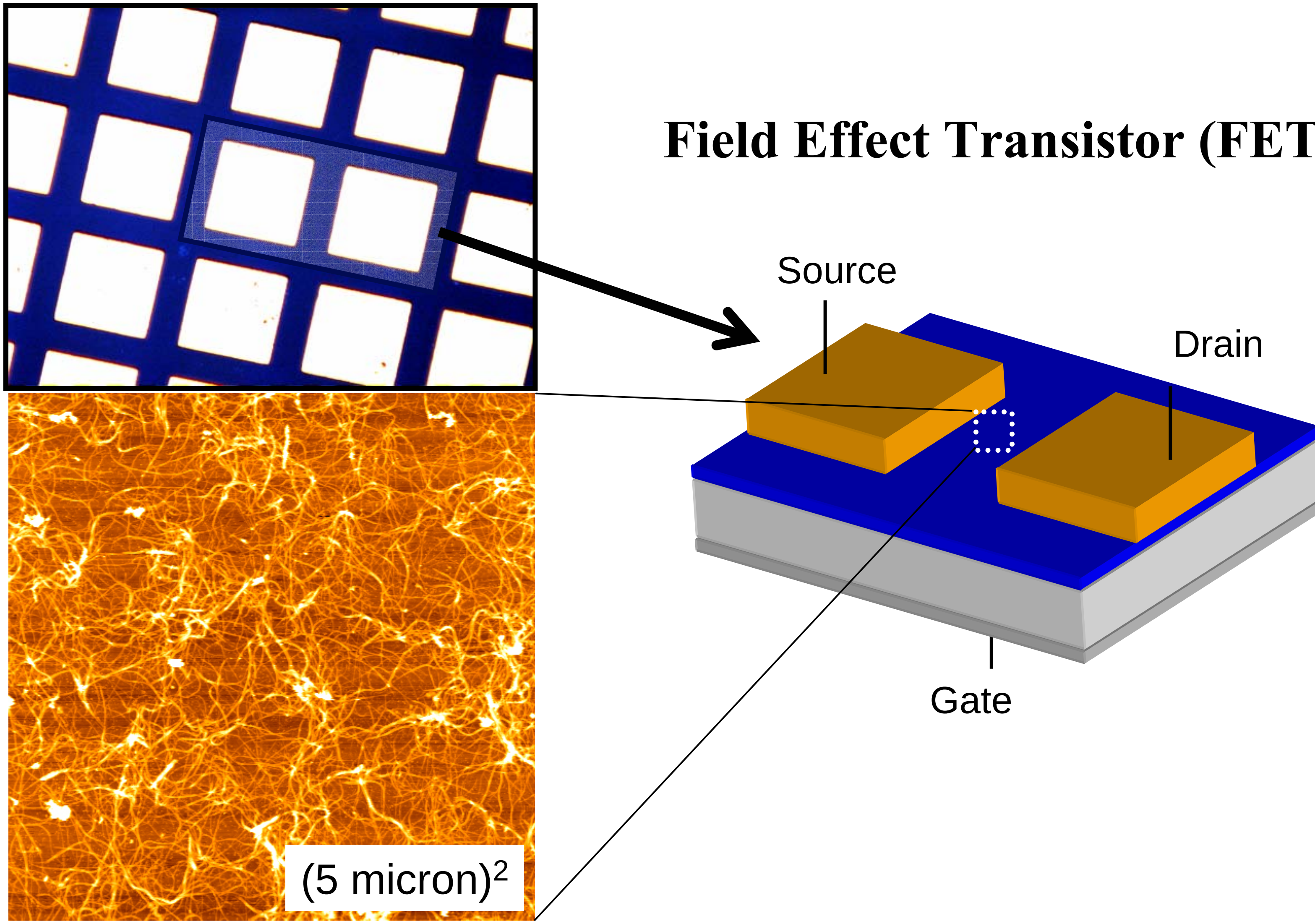


- Flexible, transparent logic using films of pure semiconducting SWNTs
- Flexible, transparent conductors using films of pure metallic SWNTs
- Multi-analyte optical / electronic sensors
- Controlled conductivity films for cell growth

Field Effect Transistors from SWNT Films

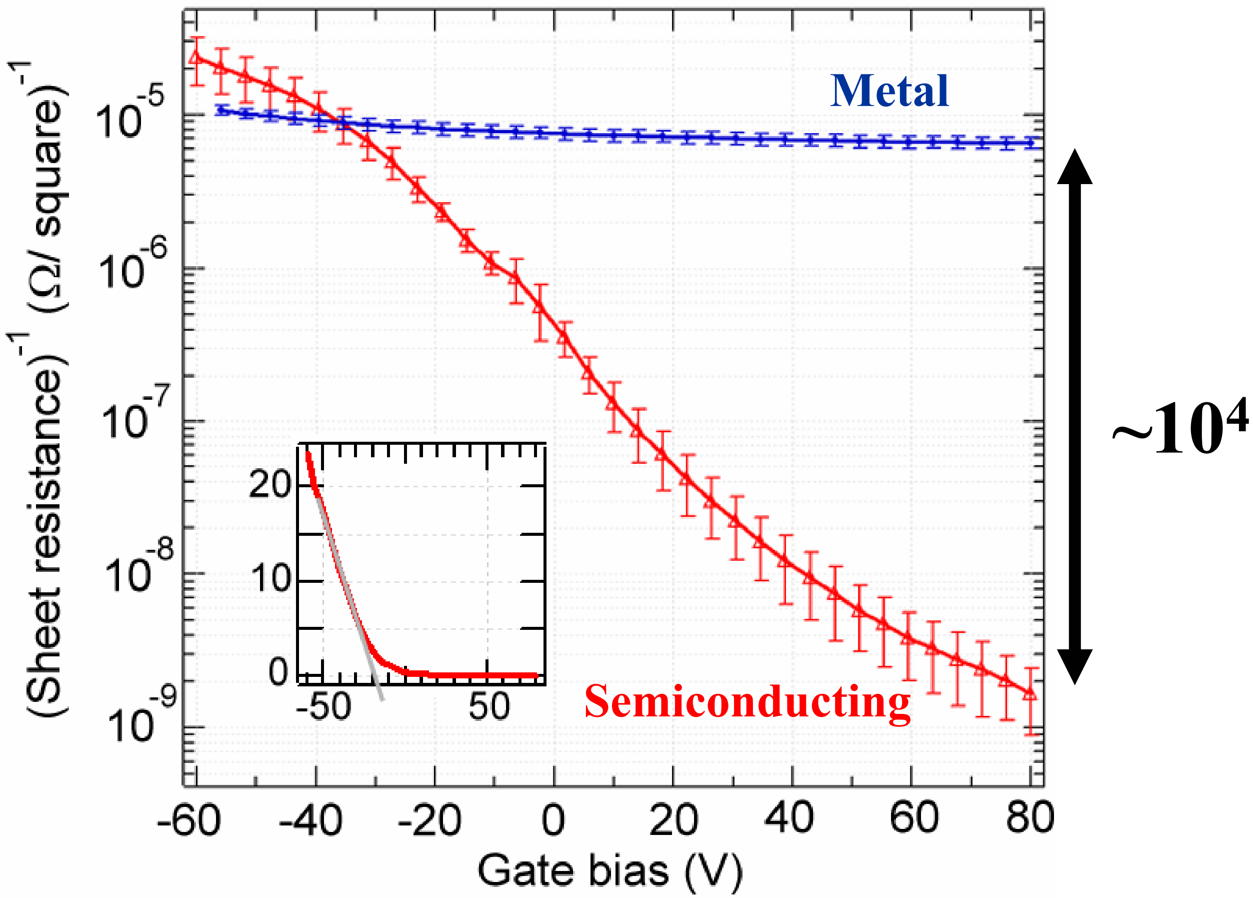
Nature Nanotechnology, **1**, 60 (2006).

Field Effect Transistor (FET):



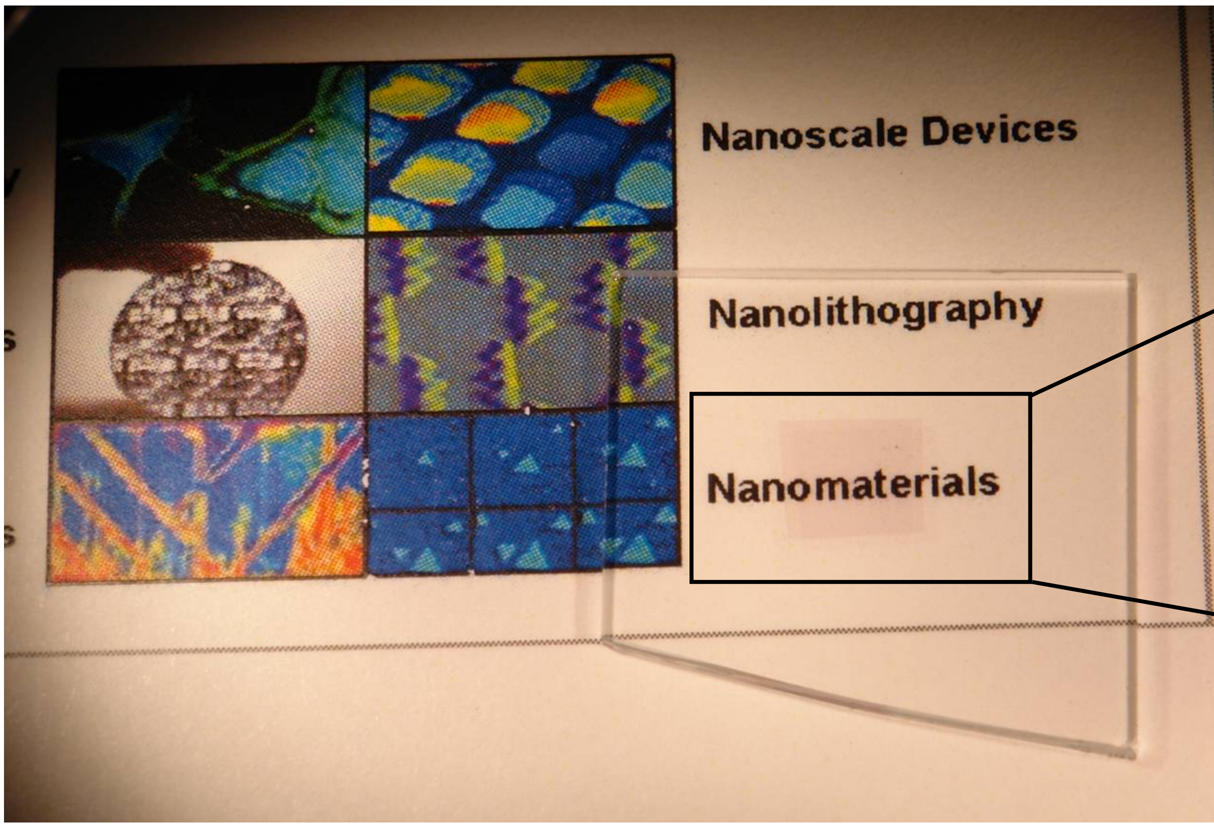
Metal versus Semiconductor FETs

Nature Nanotechnology, **1**, 60 (2006).

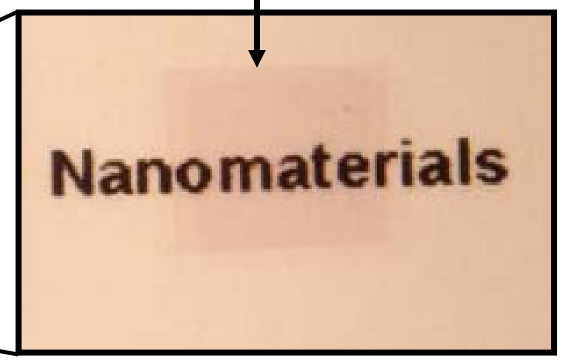


Semiconducting SWNT films: μ > 20 cm^2/V-sec

Transparent Conductors from Purified Metallic SWNT Films



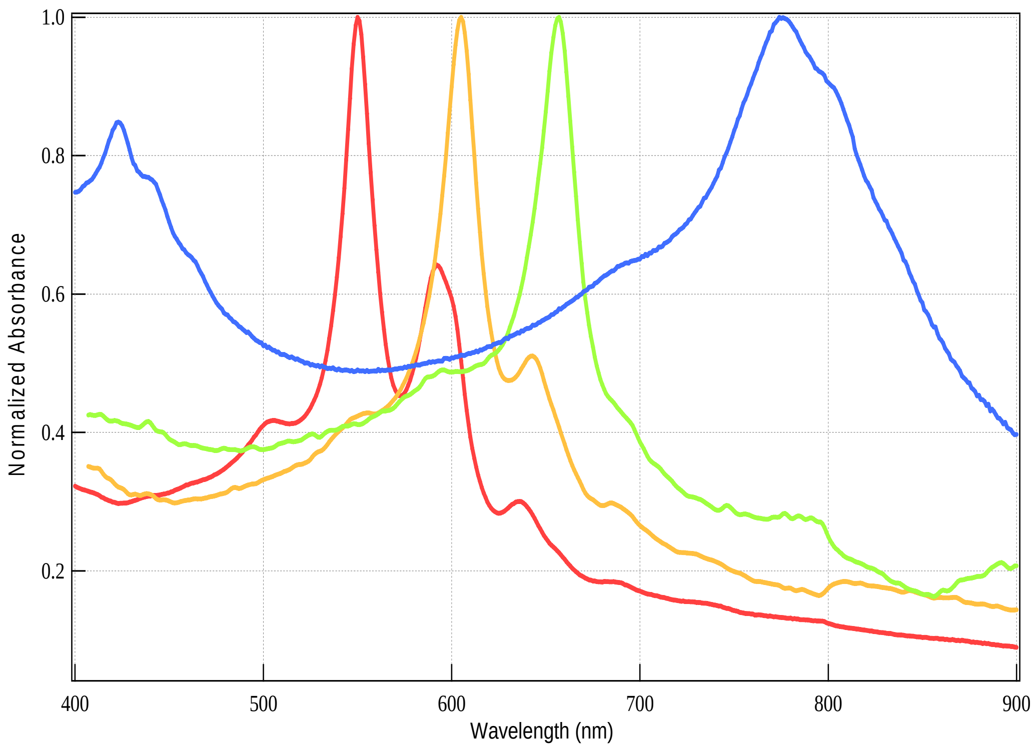
High optical transparency in the visible and the infrared



Sheet resistance decreases by ~10x when using metal SWNTs sorted via density gradient centrifugation

Diameter Sorting Enables Metallic SWNT Films with Tunable Optical Absorption

Increasing metal SWNT diameter

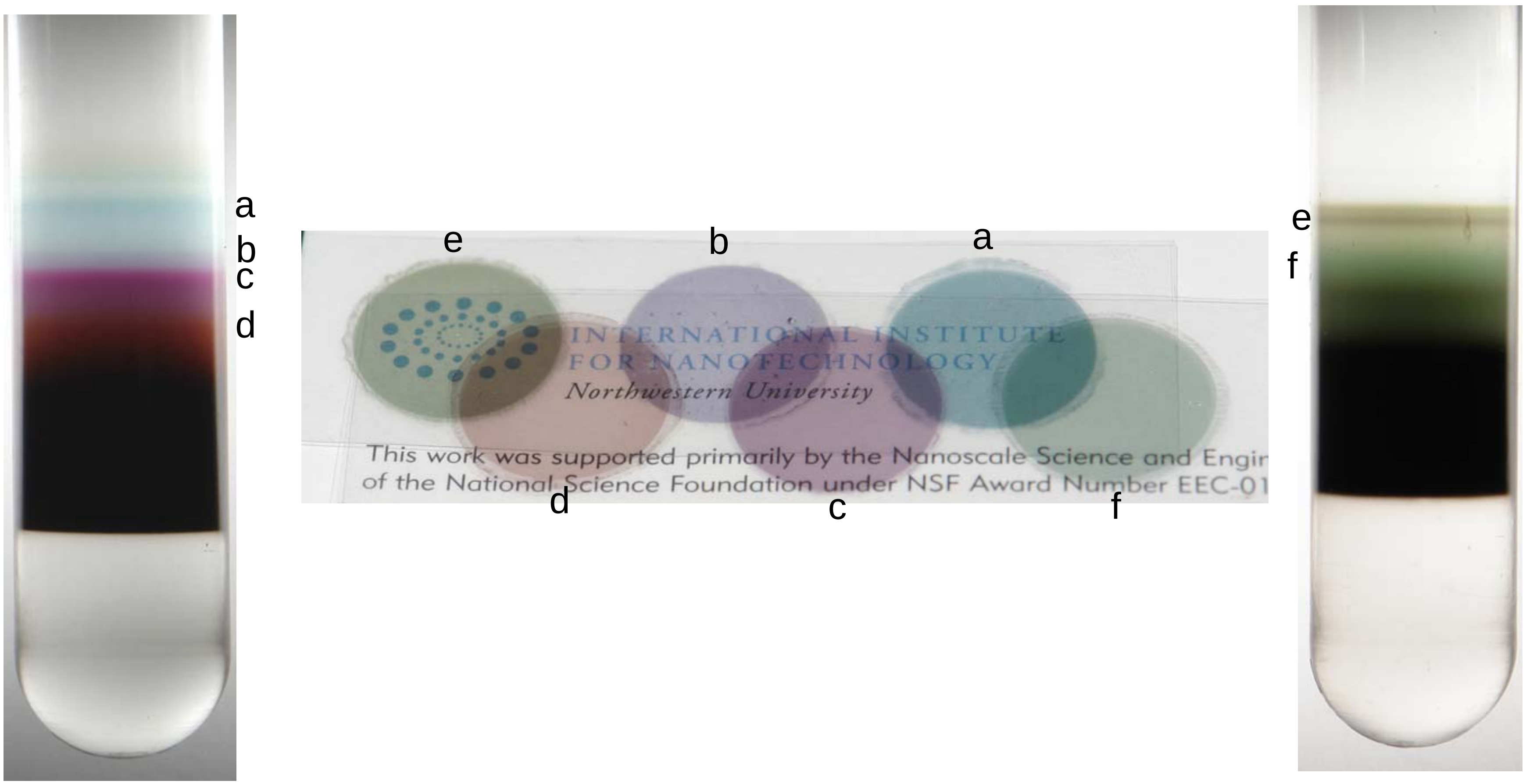


Increasing metal SWNT diameter

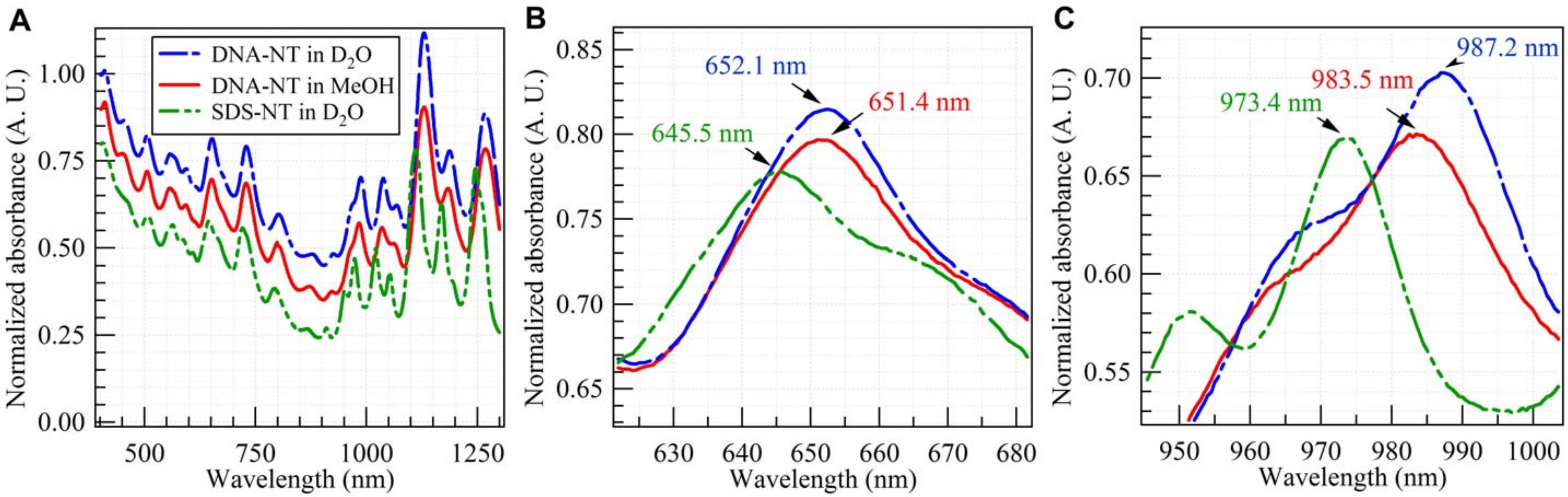
In addition, > 95 % transparency in the IR (2-2.6 μm) for sheet resistance < 100 ohms/square.

Semi-Transparent Conductive SWNT Stained Glass

- The topmost buoyant bands contain metallic SWNTs sorted by diameter
- Diameter sorting produces dramatic differences in SWNT color



Multi-analyte Optical Biosensors from Purified Semiconducting SWNTs



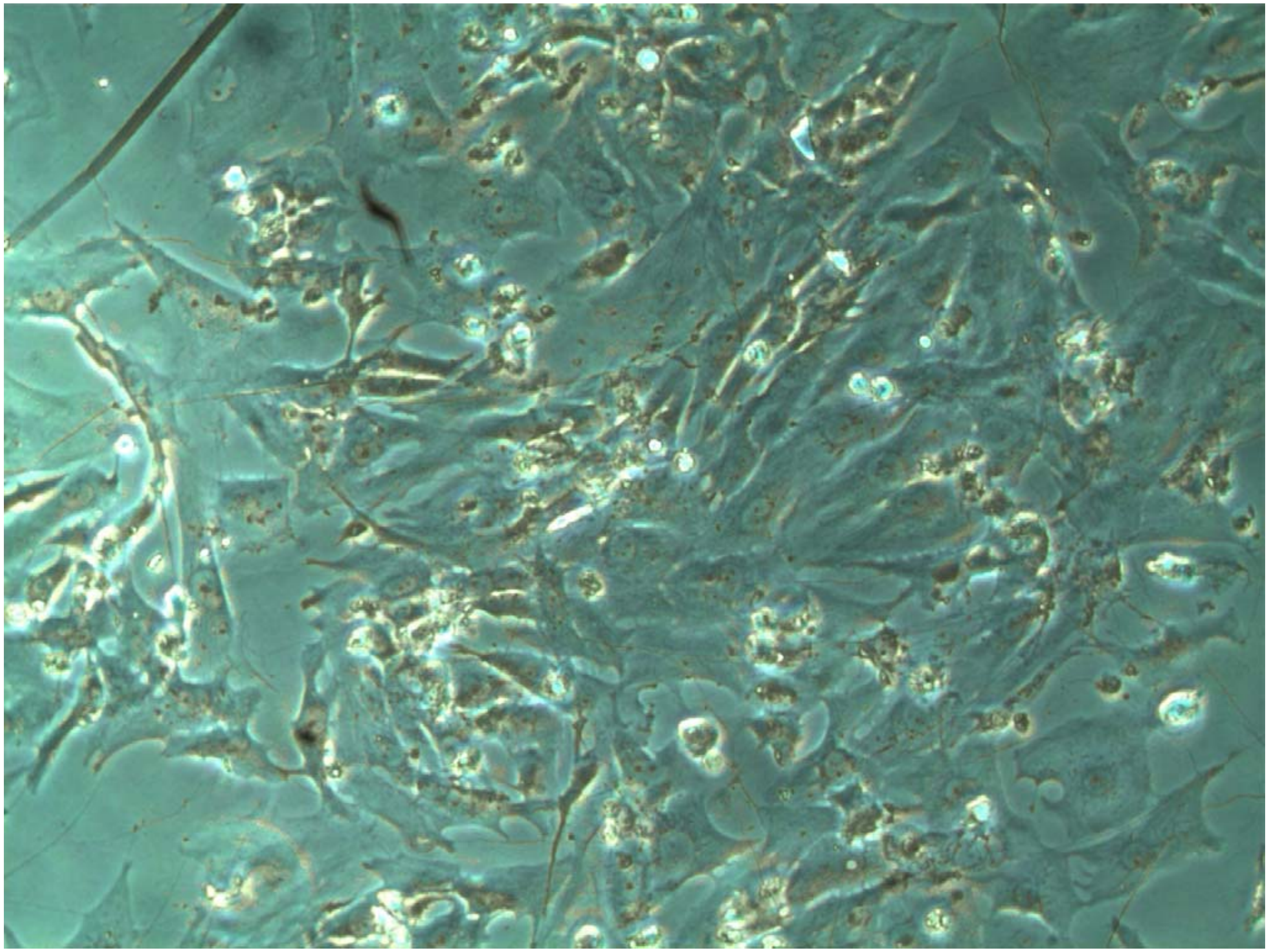
Solution	E_{11} red-shift	E_{22} red-shift
SDS-NT in D_2O	0 meV	0 meV
DNA-NT in methanol	13.1 meV	17.4 meV
DNA-NT in D_2O	17.8 meV	19.4 meV

Environment	Static relative dielectric constant
Dodecane ($C_{12}H_{26}$)	2.0
Methanol	33
Heavy water	80

- Red-shift observed with increasing external dielectric constant.
- Suggests possibility for optically based biosensors using SWNTs.

Cardiomyocytes on SWNT Thin Films

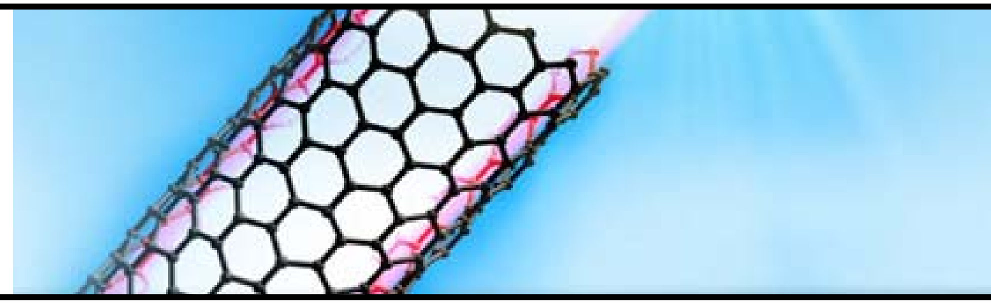
Collaboration with Samuel Stupp (NU Medical School)



Cardiomyocytes on carbon nanotube thin film after 7 days

Commercialization: NanoIntegris

http://www.nanointegris.com/



- Start-up company founded in February, 2007.
- NanoIntegris is scaling up the DGU process in an effort to bring high performance SWNTs to the scientific community.
- Product line is called IsoNanotubes™:

Product	Description
IsoNanotubes-M	Metallic SWNTs
IsoNanotubes-S	Semiconducting SWNTs
IsoNanotubes-D	Uniform Diameter SWNTs

Summary

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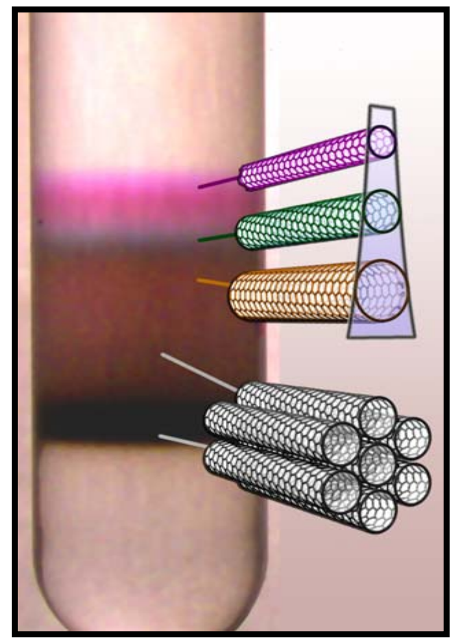

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David Comstock
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Josh Kellar
Joe Lee
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Matthew Schmitz
Tim Tyler
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Christopher Chen
Frank Du
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Shengyao Li
Christopher Liman

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